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A CONCEPTUAL MODEL FOR THE MOVEMENT OF PESTICIDES THROUGH THE ENVIRONMENT: A CONTRIBUTION OF THE EPA ALTERNATIVE CHEMICALS PROGRAM

NATIONAL ECOLOGICAL RESEARCH LABORATORY

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While rejecting formulation of a model with global validity, the authors emphasize the commonalities of the basic processes and components in the various environments. Thus, a multi-media approach to disposition studies is made explicit even in the absence of a single, all-media global model.

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CONTENTS

		Page
ABSTRACT		ii
LIST OF FIGURES		iv
ACKNOWLEDGEMENTS		vi
FOREWORD		vii
SECTIONS		
I	CONCLUSIONS	1
II	RECOMMENDATIONS	3
III	INTRODUCTION	4
IV	OVERALL CONCEPT OF THE MODEL	11
V	THE ATMOSPHERIC/TERRESTRIAL MODEL	27
VI	THE FRESHWATER AQUATIC MODEL	40
VII	THE ESTUARINE/MARINE MODEL	55
VIII	REFERENCES	59
IX	KEY LITERATURE SOURCES FOR PESTICIDE EFFECTS RESEARCH	63
APPENDIX		73

FIGURES

No.		Page
1	Variable-Form Module: Chemical	5
2	Global Array of Environmental Regions	7
3	Food Web Module	9
4	Diagram of the Atmospheric/Terrestrial Model	30
	4A ATMOSPHERE	31
	4B FAUNA	34
	4C FLORA	37
	4D SOIL and WATER	38
5	Diagram of Faunal Subsystem Model	33
6	Vertical Representation of a Stratified Lake	43
7	Horizontal Representation of a Lake	44
8	Horizontal Array of Vertical Columns for Representation of Lotic Systems	45
9	Some of the Storages, Processes, and Subsystems Associated with the Surface Layer Storage Compartment	47
10	An Expansion of the Hydrologic Input	48
11	A Skeletal Abstraction of a Food Web	49
12	Food Chain Model of DDT in a Freshwater Marsh	50
13	A Minimal Representation for a Pesticide in a Dimictic Lake	52-53
14	Simple Model of Transport in Estuaries	56
15	Expanded, Iterated Basic Chemical Module for Transport of Chemicals in Estuaries	57
	Biota-mediated Flux (overlay)	57

FIGURES (Cont'd)

No.		Page
A-1	Relationship Among Graphical Representations	74
A-2	Streeter-Phelps Oxygen-Deficient Model for a Stream	76
A-3	Vollenweider Lake Eutrophication Model	76
A-4	Nutrient Model for Lake with Biotic and Abiotic Storage	78
A-5	Possible Coupling of Biomass (B) Subsystems with Nutrient Concentration (Mb) Subsystems	79

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FOREWORD

This report is a product of the Environmental Protection Agency's Substitute Chemicals Research Program, which seeks chemical alternatives to certain pesticides. The report provides an overall view of these chemicals regarding their pathways through and possible effects on the environment. Since the substitute chemicals to be investigated may exhibit properties similar to conventional pesticides, such as bio-concentration and bio-degradation, this program was initiated to study the environmental routes and rates of transport, metabolic fate, and sinks for a variety of these substances.

Many chemicals, including the substitute chemicals, move throughout all of the environment, and their total impact cannot be evaluated by a research program dealing with only one part of the environment. Experiments designed to provide data for regulatory function must include as many parts of the environment as possible. For this reason, the whole ecosystem approach has been adopted in this program.

We have thus presented an overall conceptual scheme from which scientists, administrators, management executives, and other interested persons with a concern for pesticide-related problems can obtain an overview.

SECTION I
CONCLUSIONS

Pesticides are applied to the ecosystem of the pest and not to the pest alone. An ecosystem by definition is a causally closed system in which each process is influenced by overall system structure. The concept of the ecosystem represented simply in thought or language is of little operational use until translated into more functional diagrams. Each of the many forms of system diagrams has strengths and weaknesses depending upon their application. An iterative process of expansion and systematic reduction of components to achieve an optimal balance between resolution and effort can be employed to join various segments of the environment.

Placing the pesticide problem in the control diagram format forces the investigator explicitly to define and delimit a complex hypothesis. Further, systems analysis and simulation techniques may be applied to mathematical approximation of the hypothesis stated in the control diagram. When applied to a preliminary system diagram, these analyses allow systematic reduction to a less complex form. As a preliminary to an experimental study, these techniques can provide answers to many questions concerning the variables to be measured, the accuracy required of the measurement, and the frequency of sampling. Thus, these methods of modeling and techniques of analysis enable investigators to develop models for the behavior of a specific pesticide in a specific ecosystem yielding an approach to optimum information re resource expenditure.

Ultimately, mathematical modeling and analysis could precede introduction of chemical which might be potentially hazardous in the environment. By identifying those properties of the agent and the

systems and by quantifying interactions of components, mathematical simulation can direct critical experiments to verify hypotheses of disposition and effect. The conceptual model is the first step in a rigorous scientific treatment of the fate and effects of agents and their alternatives in pest control.

SECTION II
RECOMMENDATIONS

The conceptual model necessarily will benefit from criticism, experimentation, and utilization in research. The process of improving and updating the conceptual relationships should be a continuing function of this program.

Analysis of the disposition of pesticides in particular segments of the environment and of the effects accompanying their distribution and fate should employ the conceptual models in developing more explicit hypotheses and as an operational framework. Research in laboratory microcosm and in field validation of laboratory studies of processes, effects, etc., should be correlated through appropriate models derived from this conceptual base.

In relation to the Substitute Pesticides Program, this conceptual model should be employed in referencing the probable disposition of an alternative chemical to that of the de-registered or suspect agent that the substitute might replace.

SECTION III
INTRODUCTION

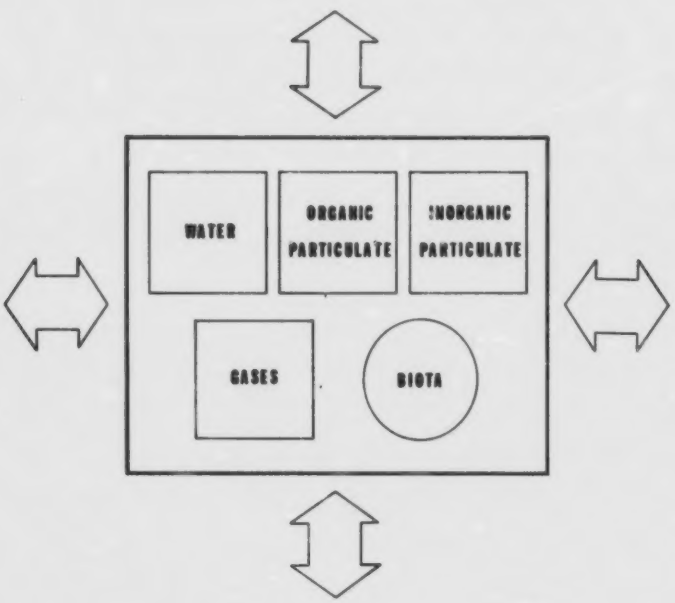
Literally millions of chemicals and combinations of chemicals are now manufactured and isolated, formulated, used, and ultimately disposed of in the environment. Management of the resources of regulatory agencies, supporting scientific institutions and manufacturers of the chemicals demands effective and reliable shortcuts in evaluating the potential hazard involved in such chemicals. The purpose of this conceptual model is to elucidate the disposition of an agent in the environment to permit judicious collection and evaluation of data that indicate the critical points in that disposition. From the conceptual model one could develop a more explicit model for the behavior and disposition of a specific chemical in a particular environment--a model that includes realistic parameters and by computer simulation provides realistic estimates of the concentration of that chemical in space and time.

A number of models have been proposed for the movement of specific agents or classes of chemicals in various environments. Some attempt to represent the global distribution of agents; others relate to smaller portions of the whole environment or to generalized segments (e.g., within man). Highly significant contributions to this effort are the works of BISCHOFF AND BROWN (1966), WOODWELL et al., (1967, 1971), HARRISON et al., (1970), NISBET AND SAROFIM (1972), KENAGA (1972), LINDSTROM et al., (1974), and ELZY et al., (1974).

In setting forth this particular set of models encompassing the atmospheric/terrestrial, freshwater aquatic, and estuarine/marine

environments, this report has established limits of validity and relevance focused locally rather than globally. The utility of the conceptual model rests in its conversion and evolution into an explicit mathematical statement capable of evaluation as a hypothesis. Current and near-future capabilities for extrinsic control of environments will limit such testing to laboratory microcosms, such as those of METCALF et al., (1971), and to small external sites, both characterizable as limited within the concepts of the model. Extension of the model conceptually in space and time can be made to the extent that the elements of the models can be grouped, subsected or interconnected.

Figure 1: Variable-form Module: chemical.
A chemical may exist "free" or "bound" in one of the states shown, all of which can interact within a region (inside box) or interact with adjacent modules of other environments (indicated by arrows).



The regional models can be considered as amplified aspects of a basic variable-form module (Figure 1) within which a chemical may exist in a "free" or "bound" form. Since any chemical may be used as a pesticide, a term describing its function, the fate and movement of any agent (and effects consequent to that disposition) can be described and displayed without regard to that extrinsic function. Thus, the model should serve not only for pesticidal chemicals, but also for other natural and man-made agents that are being evaluated. The subcompartments of modules may exist in varying proportions and with diverse relationships in different environments. Specification and elaboration of this basic chemical module are employed to relate it more specifically to a region or zone within the environment, and interrelating and interfacing such subsystems generates models of broader relevance. Subsequently, iteration of models can occur longitudinally (to represent stream flow, geographical or climatic regions, or atmospheric processes), vertically (to represent water depths, soil horizons, or meteorologic events), or horizontally (to represent distances from interfaces) to develop multi-media models.

At the interfaces of the regions explicit representation becomes most difficult. Although the models exposited cannot be viewed as globally valid, the iteration and conjunction of subsystems generate a global array (Figure 2) that serves conceptually as an overall model. As shown in Figure 2, some elements are "shared" in a more or less regular manner through seasonal, circadian, or shorter cycles and in an irregular manner through meteorologic and geologic changes. The tidelands, flood plains, and marshes are not fully represented by either aquatic or terrestrial models exposited herein, but both provide sufficient elements for subsequent elaboration as knowledge of the physical structure, physicochemical relationships, and alteration rates of these interfaces is improved. These interactions cannot be ignored simply because the mean flux appears to be zero,

because the rates of change are so slow or so fast as to lie outside apparent rate-limiting processes, or because events do not appear to affect disposition or effects of pesticides directly.

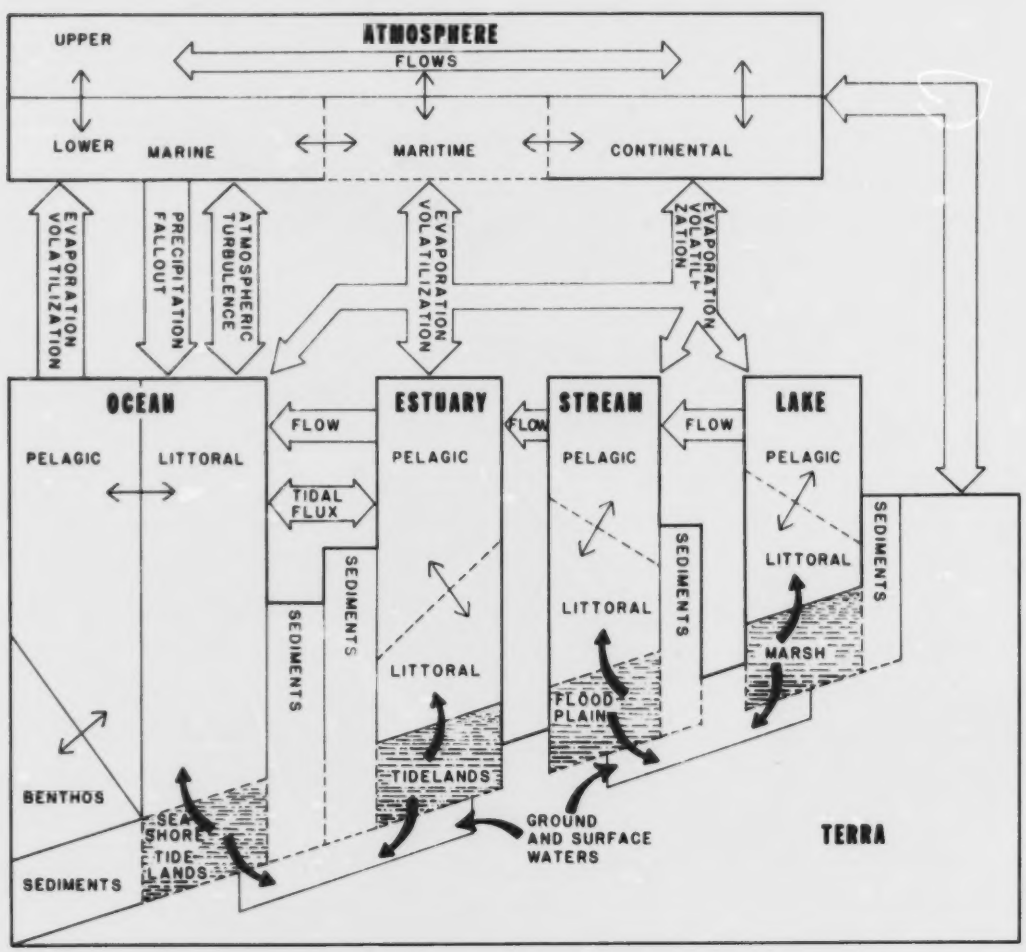


Figure 2: Global array of environmental regions. Modules can be arrayed as representing environmental regions interacting by flow (open arrows) or other transport and transfer phenomena (solid arrows) so as to represent global disposition.

A second major unifying thread of shared elements are the plants and animals designated as "Biota" in Figure 1. The interfaces of the physical environmental regions provide for considerable crossover of an agent via the biota, yet explicit representation is difficult. The phenomena of predation, migration, and vectorial transport (associated with compartmental flows) are indicated in Figure 3. Similar to the variable-form module of an environment, iteration of biological transfer and storage modules provides extension and expansion of these routes of disposition. Unlike interactions with the physical components of the environment, however, the biocidal and physiologic activities of pesticides can have pronounced direct and indirect effects on the disposition of a given agent. Determination of such effects within ecosystems would be vital to development of realistic simulation models.

Chemicals are altered by both physical and biological systems in the environment, so that site and rate of such change are highly significant aspects of the disposition. Representing these changes in a single model is difficult, especially when the agent (or its products) may alter the rate of biotransformation. Where an agent is altered chemically, we are assuming that the disposition of the product can be considered to be into a model parallel to that of the parent compound. The particulars of interaction may be describable for a given relationship, so that defined systems can be set forth for a specific chemical. In tracing the movements of an agent through this conceptual model, the products of photolysis, chemical alteration, and biotransformation can be visualized as leaving the global array (Figure 2) and entering a similar point on a model for each product. There might be many points interacting between the model of the parent agent and models of products.

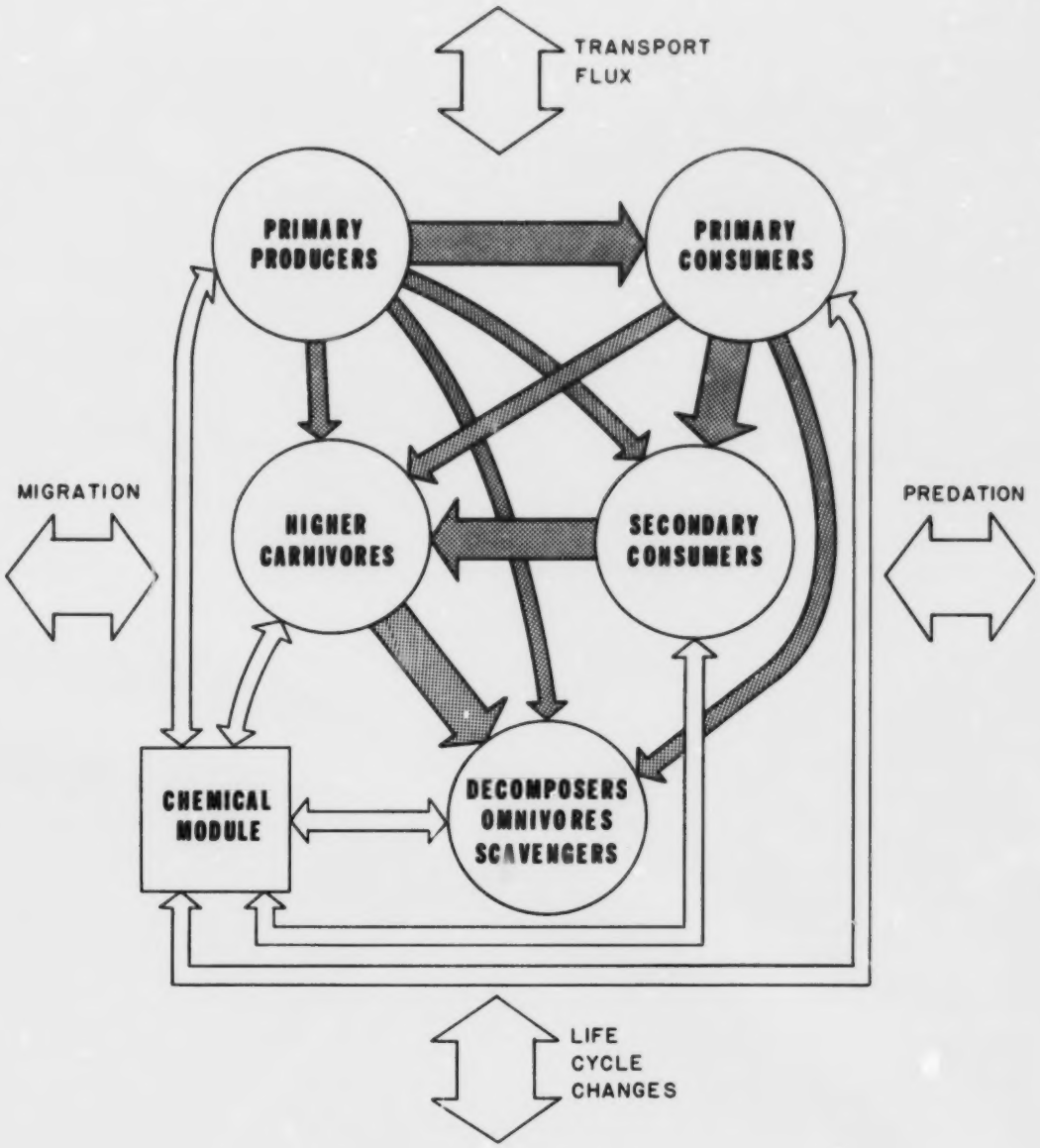


Figure 3: Food web module.
Solid arrows indicate intra-web flux by predation and feeding; open arrows indicate other transport and transfer within the food web or between food webs of different regions or zones.

Another major concept utilized in these models is that components can be represented as compartments equivalent to a well-stirred chemical reactor in a processing plant. Definition of what constitutes a compartment or component is part and parcel of the process of bringing the conceptual model into specific focus with a particular agent in a given segment or region of the environment. The extent of correspondence between (a) the definition of a "compartment" of the model, and (b) the characteristics of an environmental component determines how well a given variable-form module represents reality. Redefinition of compartments serves to make the model more sophisticated or less complicated, as knowledge is gained about the component and its functions.

The conceptual model for the transport of pesticides in the environment has been devised from three units: atmospheric/terrestrial, freshwater aquatic, and estuarine/marine. The nature of the presentations differ somewhat as expected for diverse points of reference, but the basic components and chemico-physical and biological flows are compellingly similar. This report will attempt to synthesize these components and processes further into an overall concept, then consider representations for the three major areas.

SECTION IV
OVERALL CONCEPT OF THE MODEL

An explicit, overall conceptual model derived from the principles of chemistry, physics, and biology and valid for all pesticides and environments, would over-reach the bounds of current knowledge. For practical translation into a quantitative model, the common threads of these principles and of the constituents of the environmental regions must be woven into a fabric or matrix of systems capable of analysis. Practically, we are forced to examine experimentally relatively small regions which can be characterized and/or controlled, or we must generalize these models by summation (see HARRISON et al., 1970; WOODWELL et al., 1971). Iterative simulation of the models over all environmental regions would require an unachievable data base, but much can be learned about the whole even from the parts. These will tell us where sampling and monitoring will be valid and helpful. Attention could thus be focused on the processes and mechanisms affording (and on these factors affecting) disposition.

PRELIMINARY SYSTEMS ANALYSIS FOR REDUCTION AND EXPERIMENTAL DESIGN

A diagrammatic representation of a system is usually of value to a scientific investigation even if the potential applications of the system representation are not realized. The trial-and-error expansion and reduction of compartments forces the investigators explicitly to acknowledge the boundaries and the level of definition of the system.

Deciding upon alternative representations of flow and control paths promotes consideration of even the most remote possibilities. Finally, many of the assumptions necessary to represent the system are explicit in the diagram.

The system diagram is a complex, qualitative hypothesis which must be tested by experiment. The hypothesis cannot be realistically tested in the graphical form of the conceptual models given so far (Figures 1 and 2). A more exact representation of the relationship between storages and flow rates is needed. The many possible mathematical forms for these relationships may be classified as linear or nonlinear and as recipient-controlled, donor-controlled, or mixed.

The linear, donor-controlled form (PATTEN, 1971) is probably the most elementary (CHILD and SHUGART, 1972). It can be represented mathematically as

$$\frac{dX}{dt} = AX + BZ \qquad (1)$$

in which X is a storage level vector, dX/dt is a flow rate vector, Z is an input vector, and A and B are coefficient matrices.

Donor-control implies that flow rate depends only upon the storage level from which the flow originates. Although this assumption may be unrealistic, the use of a linear, donor-control approximation of the system representation appears to be justified for these preliminary analyses. Often, linear approximations are less sensitive to parameter estimation errors than nonlinear representations. Also several expedient techniques of analysis may be applied to the linear, donor-control approximations. The following analysis techniques can yield alternative statements of the system diagram hypothesis that can be interpreted in terms of reduction and experimental design.

1. Topological analysis is currently being developed by a group of Dr. B. C. Patten's graduate students at the University of Georgia (PATTEN et al., In Press). This technique is intended to allow determination of the

influence of the topological structure on system behavior. Such information is useful in evaluating alternative system structures and particularly in determining the effects of reduction or aggregation of components.

2. Flow analysis (HANNON, 1973) or input-output analysis (LEONTIEF, 1966) is based upon the manipulation of the A coefficent matrix in the linear, donor-control approximation. Briefly, a matrix $\underline{G}$ is generated by

$$G = \sum_{i=1}^{\infty} A^i \qquad (2)$$

in which each element (G_{ij}) is a relative measure of the fraction of flow out of storage $\underline{j}$ that appears as input to storage $\underline{i}$ under steady state conditions. This information may be used to identify important processes or flow paths in the system.

3. Sensitivity analysis (TOMOVIC and VUKOBRATOVIC, 1972; PATTEN, 1973), may be used to evaluate the effect of a perturbation, $\underline{v(t)}$, upon the storage levels in the system. The measure of sensitivity, $\underline{S}$, is useful in determining which parameters have a prominent effect upon system behavior. A linear approximation of $\underline{S(t)}$ is determined from

$$\frac{d\,S(t)}{dt} \simeq \left[\frac{d\left(\frac{dX_i}{dt}\right)}{d\,X_i}\right] S(t) + \left[\frac{d\left(\frac{dX_i}{dt}\right)}{d\,A_{ij}}\right] V(t) \qquad (3)$$

where the terms in brackets are Jacobian matrices. With a unit perturbation of each parameter, A_{ij}, the steady-state values of $\underline{S}$ for each storage variable may be used as a relative measure of system sensitivity to each parameter.

4. Frequency response analysis (CHILD and SHUGART, 1972; WEBSTER et al., In Press) provides frequency-related measures of system behavior. Both the referenced papers and current studies indicate that the sampling ratio (ξ) and the undamped natural frequency (ω_n) are well described by a second-order control system approximation of the system (KUO, 1962; DERUSSO et al., 1965). When the system is overdamped (most ecosystems appear to be so), then the undamped natural frequency becomes a measure of the maximum required sampling rate for system variables.

5. Component analysis (HILL, 1973) allows numerical determination of a limited number of coefficient values from the A matrix of the linear, donor-controlled representation and the system transfer function as determined from experimental input-output data.

Topological analysis can be used as an aid in evaluating the influence of connectivity upon process rates in the system. Flow analysis can provide a measure of steady-state distribution of flow through the process pathways. A preliminary sensitivity analysis can determine the effect of an error in parameter estimation upon storage levels and hence upon flows. These three evaluations of process-system interaction provide criteria for elimination of components that have the least effect on system behavior, thus systematically reducing the graphic representation. This results in information that may be used as a first approximation in choosing measurement methods and sampling rates for evaluation of system hypotheses.

MECHANISMS OF DISPOSITION

Much of the movement and fate of a given agent is dependent on the rate and nature of certain mechanisms or processes which do not differ

in character or principle between the various compartments. Explicit in this dependency are (a) the physical, chemical, and biological principles of behavior of the chemical and environmental component and (b) the organization of the constituents as described in the diagram.

It is convenient to divide these processes into two major groups: transport processes, where the agent is moved vectorially in association with an environmental component or by mass flow and diffusion; and kinetic processes, where the movement can be described by kinetic rate constants related more specifically and pointedly to the agent. When considering distributions of a chemical with respect to time, these diverse processes may play significant roles in determining whether a given disposition is flow-limited (by transport processes), compartmentalized (by kinetic processes), or some combination of both. The reference time frame, not specified for the conceptual model, is a highly significant parameter vital in translating the conceptual model to realistic simulations. Similarly, the spacial reference point (volume, location) has purposely been left vague to permit the general case to be stated with the understanding that specification of spacial and geographic localization will be carried out in translation and elaboration of the modules (Figures 1 and 3) into models.

Examples of transport processes can be seen in dispositions primarily dependent on stream flow, surface-to-ground water flow (leaching), blood circulation, xylem transport, and precipitation from air. Kinetic process-dependent dispositions may involve high or practically irreversible sorption or binding, differential rates of sorption or desorption between compartments of a major subsystem, or differential chemical alteration. The following are offered as the principle processes limiting or affording disposition of an agent in the environment. More than one process may be occurring simultaneously along the same route, so that the factors controlling the process determine the proportion going by a particular pathway, which in turn may alter that of another route.

Transport Processes

Convective Mass Transport ("leaching," "drift") -

This physical process operates in all environments, in both the gaseous and liquid phases, usually along the direction of mass flux. In SOILS it would depend strongly on the degree of soil saturation, in the ATMOSPHERE on the micrometeorological air flows, and in the AQUATIC environment on hydrodynamics.

Inter-particle Diffusion (linear, eddy, etc.) -

This process operates where chemical gradients or local turbulence exist. Viscous solvent drag effects (included in the commonly used term "dispersion coefficient") also operate.

Intra-particle Diffusion (absorption/de-absorption) -

Fickian chemical gradients act as driving forces causing chemical mass to enter and diffuse into or out of particulate matter itself. The structure of the particle, its degree of internal saturation with water, the size and diffusivity of the chemical, and the chemical's structure are important factors. Included in this category would be "exclusion-type" processes, where pore size of inorganic particulates may be large under one set of environmental conditions (pH, degree of saturation), permitting entry of chemical to sites unexposed under other conditions, and the subsequent trapping or binding of the agent therein when the conditions change.

Co-distillation -

Volatilization in association with water evaporation takes place at the soil/air and water/air interfaces and is highly dependent on the temperature, degree of soil moisture or amount of water surface exposed, and the chemical vapor pressure.

Sublimation from a Surface -

This might be regarded as a compartment with the barrier consisting of the heat of vaporization of the component and is significant for the outer portions of multi-layered chemical adsorbed or held on a surface exposed to the atmosphere.

Ingestion (includes feeding, drinking, imbibing, inhalation, pinocytosis, etc.) -

The mass of the compartment ingested moves into biota at rates highly dependent on age, physiological and nutritional status, species, season, temperature, availability of alternative foods or sources of water, etc. Several physicochemical and biological processes may be involved with the intimate uptake (absorption, facilitated or active transport, etc.).

Kinetic Processes

Adsorption-Desorption Phenomena (phase-surface interactions) -

The principle parameters of this movement are the enthalpy of sorption of the chemical and the activation energy of the surface. Hence the structure and properties of the agent and the total surface chemistry of the interface are critical. The nature and type of surface (composition of soil, tissue of animal, type of particle) and the surface area presented to the phase containing the "free" agent are important. This process is regarded as being represented by a pair of kinetic equations, the ratio of which rate constants is the measure of the equilibrium attainable between the surface and the medium. The residence time of the medium (rate of change in compartment contact), if small in relation to the rates of these reactions, may limit disposition. Where the rate of binding exceeds very greatly the rate

of desorption, the material may appear to be irreversibly bound. Where these rates are both substantially slower than the rate of media movement, the surface interaction will characterize the disposition. Moisture level, pH, and temperature, as they affect the chemical and the surface, will play major roles in this phenomenon.

Chemical Transformation -

The non-biological alteration of a chemical introduced into any part of the environment is dependent on the moisture, pH, and temperature of that environment, on the nature of reactive groups on the agent, and on the presence of catalytic sites (on particles, etc.). The nature and intensity of illumination additionally determines photochemical reactions. At very high temperatures (pyrolysis) both physical and chemical structure may be broken down to yield material in the vapor state. In biota, soils, and water, and to a much less extent in air, cation and anion exchange capacity coupled with eletrolyte levels determines ionic interactions which may alter the structure or availability of a chemical, such as by the formation of insoluble complexes. In some instances the chemical reaction phenomena are closely associated with adsorption-desorption processes, related nonlinearly to the extent of coverage by, say, soil or air moisture of the catalytic binding site where the reaction might be hydrolysis. To the extent that the media are suitable for reaction or provide a necessary reactant (e.g., ozone) these processes can appear to be compartmentalized in rate of disposition.

Biological Alteration (includes activation, degradation and conjugation) -

These processes are assumed to be catalyzed by enzymes, although similar or identical chemical or photochemical reactions may be taking

place at the same time (at reduced rates) in the same compartment or others. The great increase in rate of the enzyme-catalyzed reaction provides opportunity for compartmental differentiation of disposition. These reactions are highly dependent on species, status (physiological, nutritional, and previous chemical history), and route of exposure. They may: provide for an agent becoming more or less biologically active; for binding or conjugation in a form more or less available to other organisms, compartments, etc., without altering the potential biological activity; or for the covalent interaction of the agent with an enzyme, thus altering the capacity of the system subsequently to carry out alterations at the same rate (inhibition).

The biological effects of an agent are difficult to separate from disposition, inasmuch as one potential effect is to alter disposition routes and/or rates. Known pesticide-induced enzymatic reactions in both vertebrates and invertebrates include oxidation-reduction, hydrolysis, conjugation, and carbon-carbon bond cleavage. The enzyme activities induced may represent de novo synthesis of theretofore unexpressed genomes (microbial) or amplification of the rate of genome expression (higher animals). Biochemical alteration of environmental contaminants and agents can be viewed as a function of the expression of genetic material in coordination with the ability of the environment and the biological species to provide for synthesis of enzyme and cofactors to support the reactions. Changes in the course of this expression may be one of the biological effects interacting strongly on the disposition of a particular chemical.

Factors Affecting Disposition

As noted in the foregoing discussion of mechanisms, the disposition of chemicals in the environment is governed by physicochemical, physical, and biologic processes which can be related to properties of the chemical

Table I. FACTORS AFFECTING DISPOSITION OF CHEMICALS IN THE ENVIRONMENT

Mechanism, Pathway, or Process	Properties of Agent	Properties of Environmental Component	Environmental Control
Convective mass transport; Inter-particle diffusion	General-association with compartmental component	Vectorial flux; degree of saturation of immobile matrix by movement	Physical (water or air flow, soil movement); temperature and gross energy distribution
Co-distillation; volatilization/ Condensation	Size, diffusion coefficient in media; vapor pressure, latent heat of vaporization; interaction with media; intra-molecular interactions	Water evaporation rate, surface area, interaction with agent, degree of soil moisture, extent of saturation of air	Temperature, energy flux
Intra-particle diffusion	Size, diffusion coefficient in particle, chemical gradient	Structure (micro), degree of water saturation, alterations of structure by temperature, pH, ionic strength	Temperature, pH, humidity or soil moisture
Ingestion	General-association with compartmental component	Nutritional value to feeder, attractiveness (chemical or physical), availability of alternative foods, degree of competition with other feeders, nutritional and physiologic status of feeder	General-biological structure of ecosystem, physical conditions affecting rate or choice of foods (temperature, season, light)
Adsorption/desorption	Structure, enthalpy of sorption (mono-layered); enthalpy of fusion (multi-layered)	Macro- and microstructure, surface area, activation energy of surface	Temperature, humidity or soil moisture, pH

Table I (cont)

Mechanism, Pathway, or Process	Properties of Agent	Properties of Environmental Component	Environmental Control
Chemical reaction phenomena	Structure (reactive groups); energy of activation, free energy of reaction, nature of mechanism	Structure (catalytic sites), energy of activation, reactive sites, degree of coupling to other systems providing reactants or removing products	Temperature, humidity or soil moisture, pH nature and quantity of light
Biological alteration (activation, degradation, conjugation)	Structure (reactive groups), energy of activation, free energy of reaction, nature of reaction mechanism, binding constant to enzymes acting on it	Genetic capacity for eliciting appropriate enzyme, nature of enzyme, species status (physiological, nutritional, psychological), sensitivity to agent (inhibition, synergism, toxicity), degree of coupling to other systems providing reactants or removing products, presence or absence of cofactors	Temperature, pH, humidity or soil moisture, biological structure of ecosystem, previous chemical history

and environmental components. Table 1 summarizes these to indicate those factors which should be known or determined in making judgments as to the probable disposition of the chemical. Obviously, all properties play some role in that disposition in the complex, real world. As modeling proceeds from the conceptual level to mathematical simulation, these values become the critical inputs, especially as the disposition is related over time.

SOURCES OF CHEMICALS RELEASED INTO THE ENVIRONMENT

Each of the major compartments of the model can receive direct input of certain chemicals as a result of the action of man. These inputs are derived from "sources," which can be defined as the places and activities leading to the release of a particular agent. A source may result in a variety of inputs into major compartments and subcompartments, and more than one source may have very similar input into a model of pesticide behavior. For example, if methoxychlor were sprayed on a forest in a diesel oil medium, this application ("source") would have inputs into the atmosphere (both gases and aerosols), on to the cuticular or dermal surfaces of biota, and on to the surfaces of soil and water. A source may be deliberate, accidental, or adventitous, but the inputs have been handled uniformly in the models.

The sources can be grouped generally according to the major compartments to which inputs are directed and according to the time frame in the history of a particular agent that it may enter a model from a source. The latter might be divided into preconsumption (synthesis and manufacture), distribution (transport, storage, consumption, application, or use), and disposal (dumping, release). A chemical plant might serve as a source of atmospheric release of a pesticide during manufacture, a site of accidental spills during storage and transportation, and then have to dispose of waste materials containing the agent in

sanitary landfill, so that it would be a source having several inputs. Other typical sources are shown in Table 2. For the purposes of models, we then should consider the specific nature of sources providing inputs into the environment.

Atmosphere

Considerable atmospheric input occurs upon application of the large class of organic chemicals used as pesticides; i.e., insecticides, fungicides, herbicides, and rodenticides. For example, DDT is commonly applied by spraying a liquid suspension or solution by aircraft or mobile ground equipment. WOODWELL et al., (1971) report that in aerial applications of DDT to forests in the northeastern United States 50 percent or less of the amount applied was deposited in the forest. The rest was dispersed in the air either in the gaseous form or as small droplets. While much of the airborne liquid droplet fraction settles to the ground nearby, a significant amount remains aloft, to become associated with other particles and distributed in the environment at distances far from the point of initial application.

Table 2. SOURCES OF CHEMICALS FOR THE TERRESTRIAL ENVIRONMENT

Phase of History of Chemical	Examples
Preconsumption	Manufacture, food processing, mining, refining
Distribution	Application of chemical in pest control, agriculture, or for public health purposes; unintentional release resulting from the use of products containing or made of chemicals which are not totally confined or immobilized; accidental spills in transport or storage
Disposal	Release of wastes in air or industrial and domestic waste water; landfill operations; incineration; dumping and discarding

The chemical input may be in the gaseous state or adsorbed onto particulates released into the atmosphere. Accidental discharge resulting from explosions, containment vessel failure, human error, or other accidents involving vehicles or devices for transporting chemicals can cause major problems in a local geographic area, but are probably minor when considered on a global scale.

Chemical input into the atmosphere through routine use of products made of chemicals not totally immobilized, either intentially or unintentionally, is of major concern. For their model, NISBET and SAROFIM (1972) had to estimate the amount of PCBs lost to the atmosphere by evaporation of hydraulic fluids, lubricants, dielectric fluids used in transformers, and various plastics which are manufactured using PCBs.

Flora

Except for the direct application of plant growth regulators and chemicals used in pest control and for other agricultural purposes, sources are generally separated from flora by atmosphere, soil, and water of the environment. With direct application, input may occur on the foliage and/or fruiting body; alternatively, soil or water applications are sources of indirect inputs.

Fauna

As with flora, few sources directly input into these compartments. Medical and veterinary application of drugs and medicines, cosmetic and hygienic dermal applications, and consumption of food and non-food items constitute typical types of deliberate exposure from sources. In occupational use and, to a lesser extent, the general public, exposure can occur by direct inhalation of vapors or absorption through the skin. Hence, concern has been evidenced for

workers breathing or otherwise coming into contact with chemicals present at relatively low concentrations for long periods of time or at relatively high concentrations intermittently for short periods of time. Direct or indirect application of chemicals to flora or fauna can constitute a significant input for animals higher in the food chain if residues of the chemical or its alteration products are retained in the food.

Inadvertant and accidental release or even purposeful misuse or abuse of various chemicals and chemical products can also be a serious and significant direct source of agents to fauna. While some such sources are moderated through the atmosphere, soil, water, or flora, opportunities arise for direct inputs to fauna under some such circumstances.

Soil and Water

Many of the direct introductions of pesticides into the environment are sources closely connected to the soil and water regions. Application of pesticides and fertilizers by spraying a solution, liquid suspension, or granular formulation are important inputs to the soil surface, subsurface and the aquatic surfaces on both a local and global scale. In addition to adventitious contamination by accidental spills, other usages, and leakage from sources, a local region becomes a source by dumping or discarding material or by creation of sanitary landfills. Since the latter are generally of greater scope, the subsequent infiltration by rainfall and movement of surface or ground water can be major inputs throughout the soil, as detailed by ELZY et al., (1974).

Once a chemical is introduced into the soil and/or water environments, those compartments may continue to act as a reservoir for long periods of time, leading to transfer of an agent to flora and fauna. Depending

on the time rate of change of the concentration of a chemical at a site of localization, the compartment may act as a "sink" (where an agent is effectively withheld from participation in the system) or as a "reservoir" (where flows and transfer permit participation). From the point of reference of a given species, a compartment may be either a reservoir (and thus a "source" of an input) or a sink. A breakdown product (such as DDE from DDT or methylmercury from mercury) may arise in the soil and biota and subsequently appear broadly in the environment, even though it was not manufactured or synthesized as such. Thus, as the ultimate repository of waste, unwanted materials, and the products for which the chemicals were manufactured or prepared, the SOIL and WATER have pervasive major inputs into other segments of the environment.

SECTION V
THE ATMOSPHERIC/TERRESTRIAL MODEL

The model consists of a set of assumptions derived from experiment, experience, and physical law that are set forth graphically to illustrate the principal components ("compartments") of the system, the means by which the chemical itself or the components bearing the chemical being modeled move or change in the environment, and the relationships between compartments vis-a-vis this movement. Also enumerated and elucidated are the factors affecting these routes, such as the characteristics of the chemical and compartment.

ASSUMPTIONS

1. Elements or components of the terrestrial environment considered are confined in a geographic and geophysical sense to a local environment consisting of "ATMOSPHERE," "SOIL and WATER," "FLORA," and "FAUNA."

2. These elements and their constituent aspects can be set forth as compartments, representing chemical reactors.

3. The model is directly applicable only to the agent; its breakdown products or metabolites are representable as parallel models following identical conceptual functions of disposition.

4. The interrelationships of compartments and the movement of chemicals can be represented by a chemical process flow sheet.

DEFINITIONS

1. ATMOSPHERE. The gaseous phase containing suspended aerosols and particulates above the earth and its biota.

    a. Troposphere. The portion of the atmosphere in direct contact with soil, water, and the biota.

(1) Suspended particulates. Solid matter, including certain microscopic biota, suspended in the atmosphere. Each particle has a surface subcompartment.

(2) Aerosols. Microscopic matter (solid or liquid) dispersed in the atmosphere, each with a surface subcompartment.

(3) Gases. The gases and vapor-phase components of the atmosphere.

b. Stratosphere. A compartment above the troposphere and below the mesosphere having components as in (1-a), but not interacting directly with the earth and its biota.

c. Mesosphere. A compartment below the mesopause and ionosphere and above the stratosphere having compartments as in (1-a and b), but not interacting directly with the earth except through the troposphere and stratosphere.

2. FAUNA. Biota excluding plants and microorganisms (except protozoans) and including not only the terrestrial surface species but also those living predominantly in the atmosphere and in the soil.

a. Man. Human beings representable by a subsystem of several compartments based on anatomical and physiological characteristics.

b. Higher carnivores. Those creatures feeding on primary carnivores (and perhaps in some instances on forms lower in the food web).

c. Primary carnivores. Those species feeding predominantly on herbivores and (to a lesser extent) primary producers.

d. Herbivores. Those species feeding on primary producers, usually plants and related microorganisms.

e. Soil-organisms. Those primary producers dwelling predominantly in soil and the scavengers of the plant and animal matter constituting the organic matter of soils.

3. FLORA. The biota including largely the photosynthetic primary producers consumed by man, herbivores, and soil organisms. Generally the plant is represented as having a subsurface portion (consisting of subcompartments for the root tissues and potential storage or fruiting bodies) and a surface portion (consisting of foliage and fruiting body), all surrounded by a cuticular compartment.

4. SOILS AND WATER. In addition to soil organisms (2-e), this compartment is separated into two regions containing the same components.

a. Surface. The top portion of the soil, capable of interacting with the air directly.

(1) Surface water. The result of precipitation, ground water springs, etc., but distinct from streams, ponds, lakes, etc. (parts of the AQUATIC model); includes "free" water associated with soils and all solutes.

(2) Organic particulates. Colloidal materials in suspension including organic matter and decaying material derived from biota.

(3) Inorganic particulates. Inorganic soil structural materials (clay, silicates, minerals, etc.) and those insoluble materials of non-biological origin.

b. Subsurface. Similar to (4-a) but containing the ground water and associated soil water. Actually there exists a series of parallel plates or zones through the soil profile which will differ in composition, environmental condition, etc. The subsurface region indicated in this model is considered to be all that below the immediate surface in contact with the atmosphere.

PATHWAYS

The foregoing compartments are displayed in Figure 4. A compound introduced into the ATMOSPHERE (Figure 4A) may be in the vapor phase, as an aerosol, or in the form of a large particle. Chemicals in the vapor phase would be expected to adsorb reversibly to the surface of aerosols and other particulates, where the potential for alteration by chemical or photolytic means (due to catalytic sites thereon) is much greater than in the vapor phase. The particles might condense or break down, and chemicals would be redistributed. A chemical on the surface of a particle or aerosol could absorb reversibly into the particle, where photolysis would be very much less likely. All of these interactions would be taking place in the Mesosphere and Stratosphere as well as the Troposphere, which are mixed by diffusive and meterological conditions and events. Photolysis would be expected to

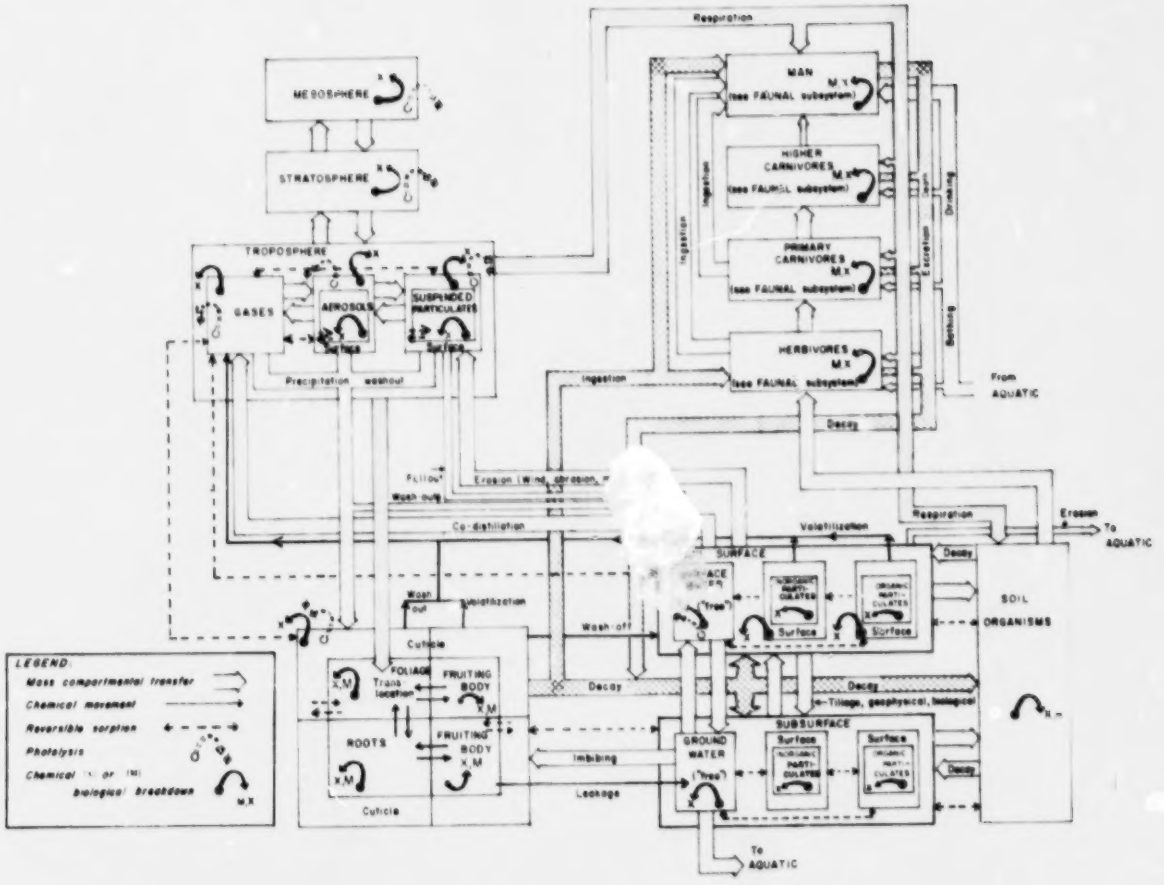


Figure 4: Diagram of the Atmospheric/Terrestrial Model.
Flow and transfer functions are indicated by the legend. Focus on segments or major compartments of the model is provided by expanded views in Figures 4A-D.

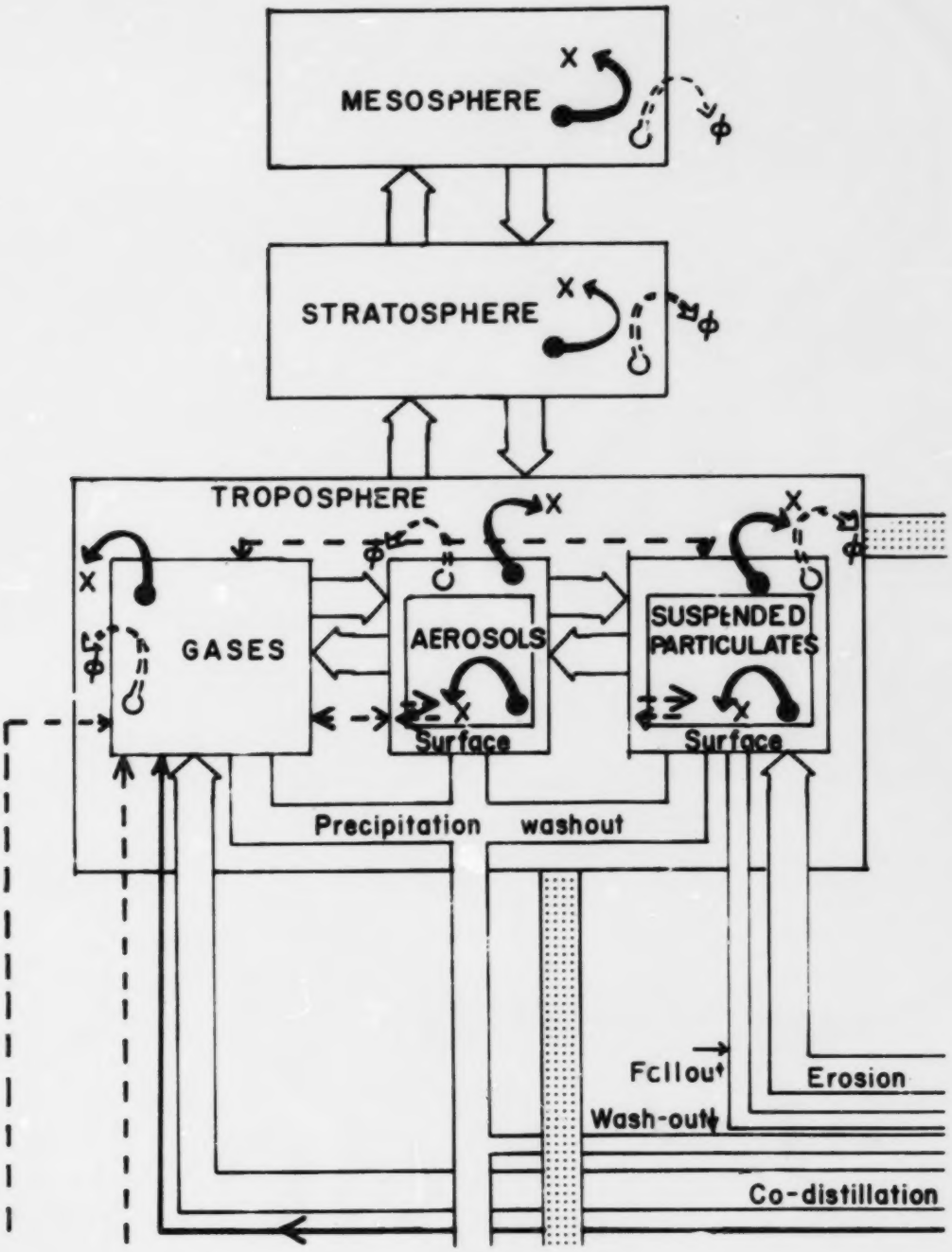


Figure 4A: ATMOSPHERE

play a progressively great role in the upper atmospheric compartments and, conversely, chemical reaction (except for ozonolysis) would be expected to be of less importance in those upper compartments. Iteration of the basic Troposphere model through the upper atmospheric compartments is easily accomplished.

Materials can enter or leave the atmospheric compartments by reversible sorption, interacting especially with SOIL and FLORA surfaces, or by volatilization/condensation from these surfaces. Particulate matter would settle out onto surfaces or be washed out by precipitation. Winds, mechanical action (such as abrasion), various modes of direct introduction (application, emission sources), and meteorologic aerosol formation in association with codistillation would result in particulate aerosol introductions into the ATMOSPHERE.

FAUNA, and to a lesser extent FLORA, would be subject to ingestion of portions of the tropospheric compartment by respiration, while sorption would provide dermal exposure. Inhaled particles not trapped in lungs, spiracles, etc., and particles or aerosols trapped on skin, hair, etc., and thereby subjected to grooming (e.g., fur licking), may be ingested with mucous. Air is also present in soils, in equilibrium with the soil surfaces *re* any component chemical; it likely plays little role *per se* in exposure of Soil Organisms and is therefore ignored. Depending on atmospheric mixing and soil movement, the exposure of Soil Organisms may be qualitatively and quantitatively different than the exposure of surface FAUNA via the air.

A schematic faunal subsystem (Figure 5) illustrates the probable inputs and outputs of the several compartments in Figure 4B (compare to Figure 3). Depending upon the food source, material from one or more of the other major compartments may be ingested, exposing the lumen tissue to the chemical in the food, air, or water. It may be sorbed, broken down within the lumen, and/or passed out with the

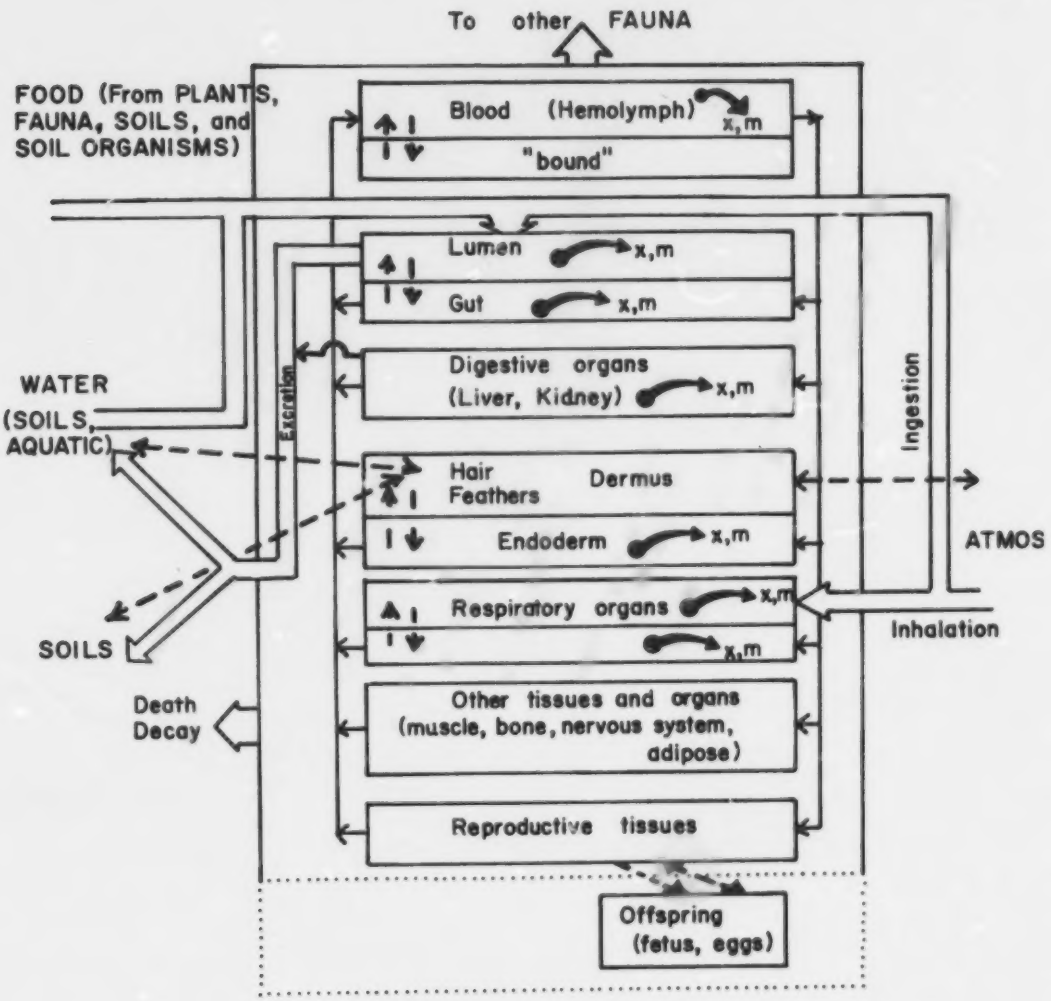


Figure 5: Diagram of Faunal Subsystem Model. (Based on BISCHOFF and BROWN, 1966). Arrows indicate flows or transfers of agent and/or compartment mass.

fecal matter, which then passes on to the SOIL or as food for other FAUNA. The portion absorbed may be distributed throughout the organisms to other tissues, which may alter the agent's structure to more easily excreted products, store the agent (for later release or for ingestion by a predator species), or provide for the agent's excretion.

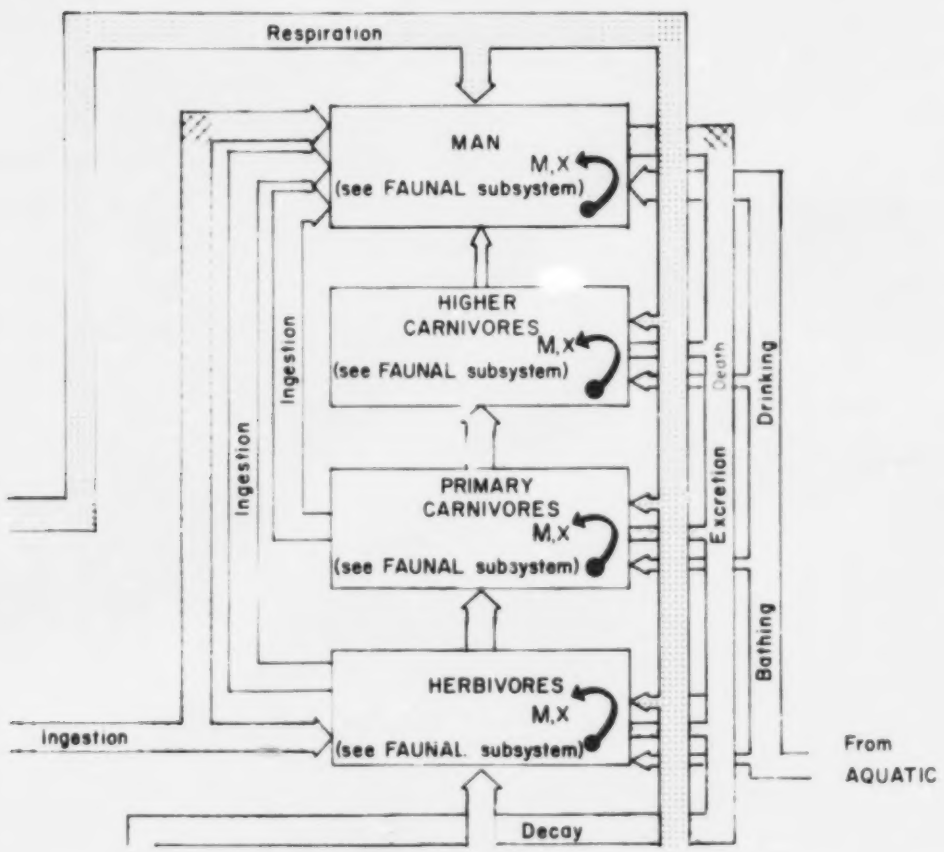


Figure 4B: FAUNA

In the higher vertebrates this process is complicated by functions such as the enterohepatic cycle (gut → liver → bile → intestinal lumen). In higher animals material may be lost through the skin, hair, or feathers. As noted earlier, these tissues also receive exposure from the ATMOSPHERE (and some instances SOIL). Some agents may be altered externally and some may not penetrate the dermal barrier. Unabsorbed material could volatilize or be adsorbed by atmospheric particles. Except for exhalation of unadsorbed material, pulmonary losses of chemicals taken into animals by other routes appear negligible.

Agents are also distributed to reproductive tissues, which can constitute a major outlet of chemical for the exposed animal. In female mammals this release can continue on through parturition into lactation. The route to offspring may be of great significance, since the young of many species serve as food for higher trophic levels.

Another major loss route, in addition to excretion, is the death and decay of tissues and organisms, leading to the entry of the material into the SOIL and WATER compartments (Figure 4D). Initially on the Soil Surface subcompartment, these materials become part of the organic particulates and later free water of that compartment, but are transferred by mechanical, geophysical, and biological action into the Subsurface compartment. Soil Organisms then ingest these particles, and one could propose an elementary version of the scheme in Figure 5 for disposition of the chemical in those organisms. Additionally some Soil Organisms may be purged of some chemicals by reversible sorption of materials in the gut lumen onto the out-going soil particles.

The other major biological compartment is that of FLORA (Figure 4C), represented as a generalized model with both Subsurface and Aerial

portions surrounded by a waxy cuticle. Materials can be deposited on this latter surface by fallout or precipitation, by condensation, or by reversible sorption. Some agents can pass on through into plant tissue or may be broken down chemically or photolytically on the surface. A portion may be washed off the leaves and added to the SOILS compartment. Material bound to the foliage will subsequently enter litter as decay occurs. An agent on the foliage may be volatilized off or sorb onto air particulates.

In the Subsurface zone, material may be brought into the plant by uptake of water or by sorbtion onto the root surface and subsequent penetration of the cuticle. Some may "leak" out or be released to the SOIL from the cuticle. Both the Aerial and Subsurface portions of FLORA are subject to herbivorous feeding, moving material into the Soil Organisms and other FAUNA, and an agent in either compartment is subject to chemical or biochemical alteration. Once an agent is in FLORA, it may be translocated to other tissues, including fruiting bodies associated with either portion. Similar to animals, a given species of herbivore may select only a limited tissue on which to feed; all portions of a plant are seldom ingested by a single creature at one time. Distribution within the plant of a given agent would therefore have a very marked effect on the subsequent nature and extent of movement of a chemical from FLORA to other major compartments. All of these movements would be less complex in photosynthetic microorganisms.

"Bound" agents, including material strongly sorbed (seemingly irreversibly) and material covalently reacted (but bearing the active groups intact) are difficult to define and determine. Some of the "bound" residues may be released by extraction, when sorption is reversed, or by chemical or enzymatic treatment, where the conjugating bonds are cleaved. In both FLORA and FAUNA (including Soil Organisms) materials considered metabolized or altered so as to leave the scheme may re-enter a compartment as a result of such action.

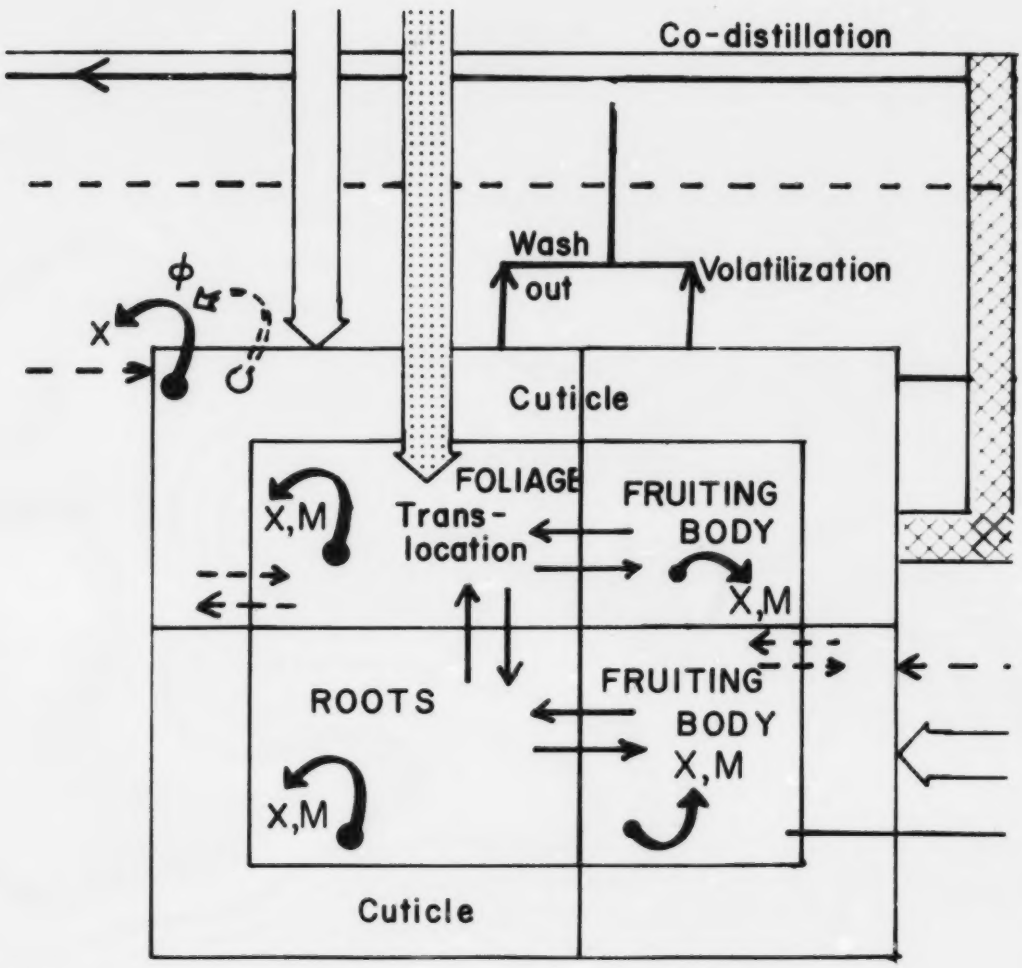


Figure 4C: FLORA

The most complex and probably most significant compartment in the disposition of an agent entering the terrestrial environment is that of SOILS and WATER (Figure 4D). Material can enter this compartment directly at the Surface by sorption from the ATMOSPHERE, condensation,

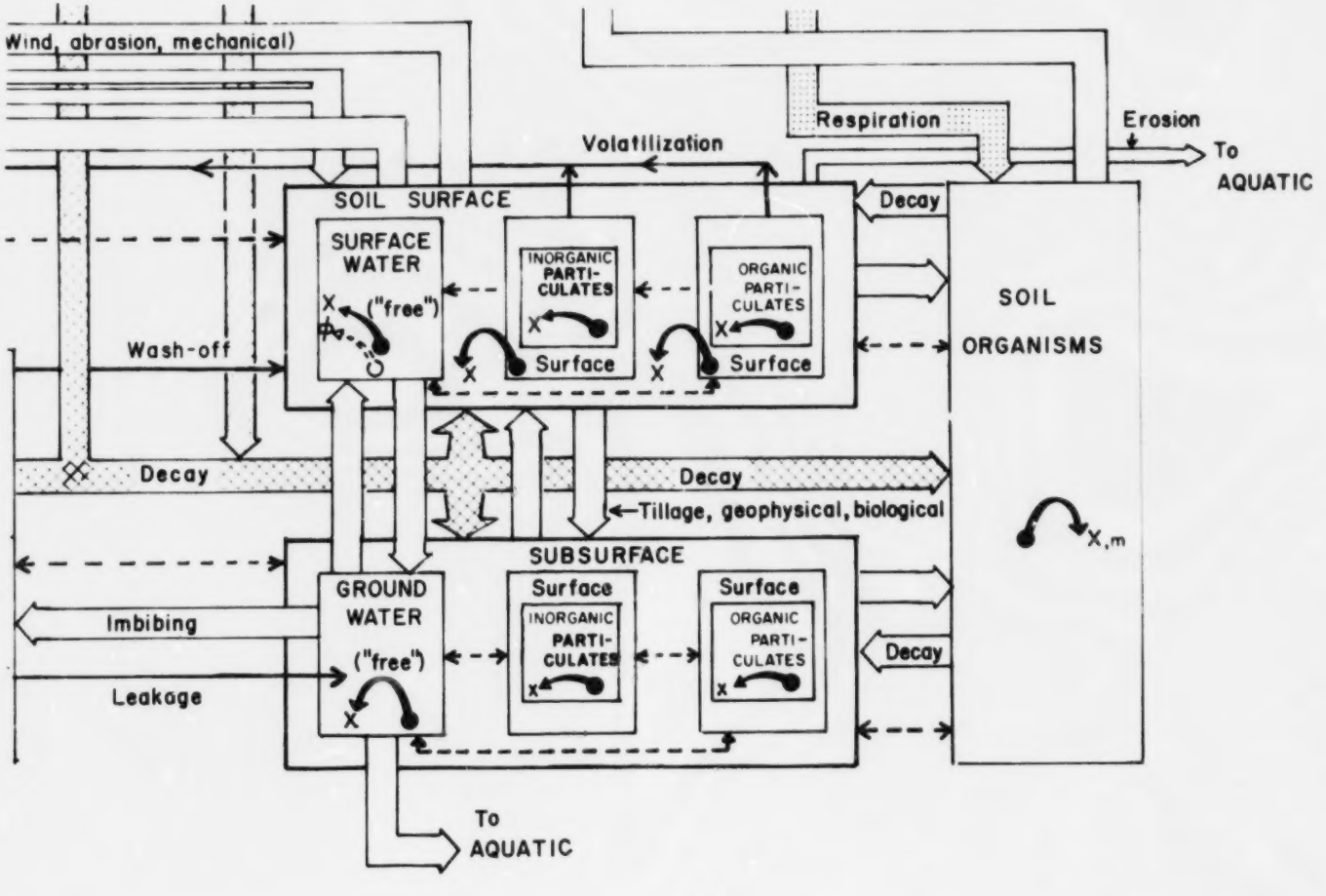


Figure 4D. SOIL and WATER

settling and fallout, and precipitation (including material washed off of plant surfaces). Excretion, exfoliation, and decay of animal tissues and defoliation, withering, litterfall, and subsequent decay of plant materials add to the routes of entry. Material can leave the Soil Surface by erosion (wind, water, or mechanical), by volatilization, by photochemical and chemical alteration, and by ingestion by Soil Organisms and other FAUNA. Some material is lost from the Surface by tillage, mechanical mixing (geophysical or biological), and "leaching." The movement of Surface water into the Ground water takes with it solubilized and reversibly sorbed materials. Within the Surface compartment, much as in the case of the Troposphere, materials can be bound to the surfaces of particulates. Surface waters can become contaminated by a Ground water-source containing an agent, which would then be distributed in the Soil Surface.

In the Subsurface zone, material can enter from the Soil Surface, be brought into the zone by Soil Organisms or FLORA (through translocation, leakage, and root decay), and can leave by routes noted earlier--sorption into FLORA and Soil Organisms (and to a lesser extent, other FAUNA), ingestion by Soil Organisms and FAUNA, and through the Ground water into FLORA and out into other waters (streams, lakes, estuaries--labeled AQUATIC). In actual cases, it would be necessary to characterize each soil horizon by iteration of interconnected Subsurface models.

SECTION VI
THE FRESHWATER AQUATIC MODEL

This section develops a systematic approach to an optimal representation of the behavior of pesticides in aquatic environments. A quantitative discussion of processes and parameters important to the fate and transport of pesticides-in-general is futile because of the diverse chemical and physical properties of pesticides. This is further complicated by the need to specify chemical, biological, and physical characteristics of the aquatic ecosystem. Therefore, a qualitative approach to studying and modeling the fate and transport of pesticides in aquatic ecosystems is discussed.

There has been a shift in many areas of science toward studies of wider scope. This has been brought about partly by increased emphasis on "the environment" and partly by wider knowledge of the techniques of system studies. According to MOORE (1967) the emphasis in pesticide studies has shifted from

Pesticide → Pest

to

Pesticide → Ecosystem

Past pesticide research resulted in few system studies and fewer mathematical analyses of such studies.

One area of system studies is that of microcosm or partial system studies (METCALF et al., 1971). These studies emphasize a particular short food chain largely as an index for comparison of various studies. Their quantitative applicability to real-world ecosystem is therefore limited. Nevertheless, they provide the basis of a large portion of our comprehension of the behavior of pesticides in the environment.

Global model studies are important in setting an overall framework within which smaller system studies may be placed. RANDERS and MEADOWS (1971) studied the movement of DDT in the environment, and WOODWELL et al., (1971) made a similar study. An important conclusion of both these papers was that the DDT concentration in food chain organisms would continue to increase long after the rate of application was decreased or terminated. This conclusion was based on computer simulation studies and comparative analyses.

Smaller system studies of greater detail bring us closer to interactions at the ecological level. Analyses of pesticide transformations and transports at the ecological level may make use of both ecological theory and various applications of systems theory. For example, EBERHARDT et al., (1971) applied system simulation to a field study as an aid in interpreting the data.

The above examples deal with specific pesticides in relatively defined ecosystems and are not generally applicable to a description of fate and transport. The presentation that follows is applicable to pesticides and aquatic ecosystems in general but can also be used as a starting point for any specific pesticide and system.

SKELETAL DIAGRAMS FOR A PESTICIDE IN THE AQUATIC ENVIRONMENT*

The most effective aggregation of storage components and rate processes varies as attention is turned from one aquatic regime to another. Even within the range of lentic systems, the diagrammatic representation for a deep dimictic lake would be inappropriate when used for a freshwater marsh. For this reason, several basic frameworks or skeletal models without detailed process embellishment are presented for different aquatic environments.

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*See Appendix for detailed background.

The first skeletal diagram in Figure 6 is intended for a dimictic lake in which process dynamics are affected by the presence of a strong thermocline. The division between epilimnion and hypolimnion may allow for long-term storage and release from the sediments of the reduced forms of some chemical species (HUTCHISON, 1957; O'MELIA, 1972). The surface layer is isolated as a storage component in this vertical model because of the possibility of enrichment in heavy metals and pesticides (DUCE et al., 1972) and the neuston food web. The sediments are treated as a separate storage unit because of possible long-term storage (AHR, 1973), sorption-desorption process rates (HUANG, 1971) and the benthic food web.

A similar vertical skeletal structure without the hypolimnion may be used for a holomictic lake or a freshwater marsh. However, a shallow lake or a marsh may be better represented by a horizontal structure (SCHINDLER, 1974) as presented in Figure 7. Here the storage is divided among aquatic communities, which have varying response times and process rates.

The independent variable implied in both of these lake models is time. However, either one may be used as a two-dimensional stream or river model by choosing longitudinal distance (i.e., downstream) as the independent variable and including hydraulic and morphologic effects on settling and mixing.

Finally, the lotic system may be represented by a horizontal array of vertical column structures (similar to that of Figure 6) with longitudinal distance as the independent variable. The transfers between columns represent the transverse mixing in the system (HOLLEY and ABRAHAM, 1973). This concept is presented in the diagram of Figure 8.

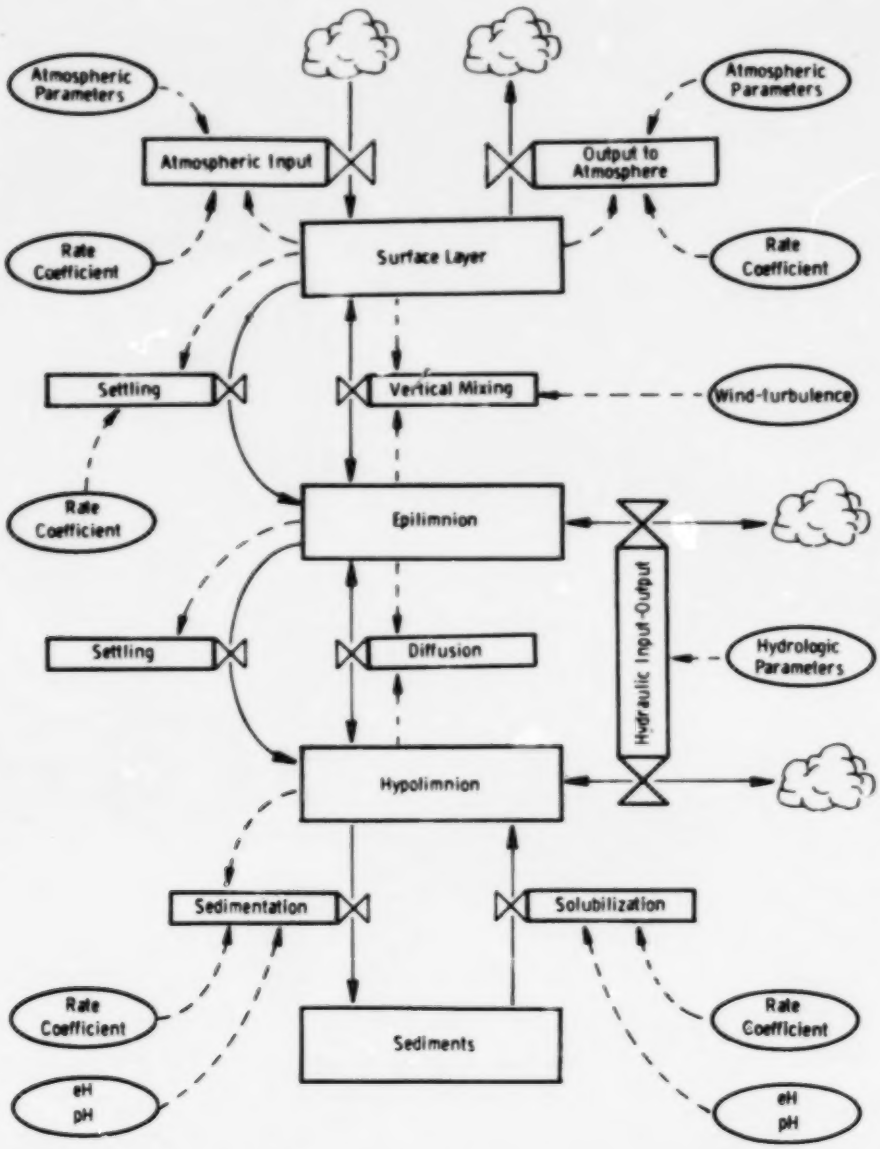


Figure 6: Vertical Representation of a Stratified Lake. Solid line - pathway of transfer of matter or energy; dashed line - control pathway of information transfer; cloud symbol - sink or source external to system boundaries; rectangle - storage of matter or energy; valve symbol - rate-controlling parameter or force; and circle - coefficients and parameters affecting flow rates. (Similar for Figures 6-13.)

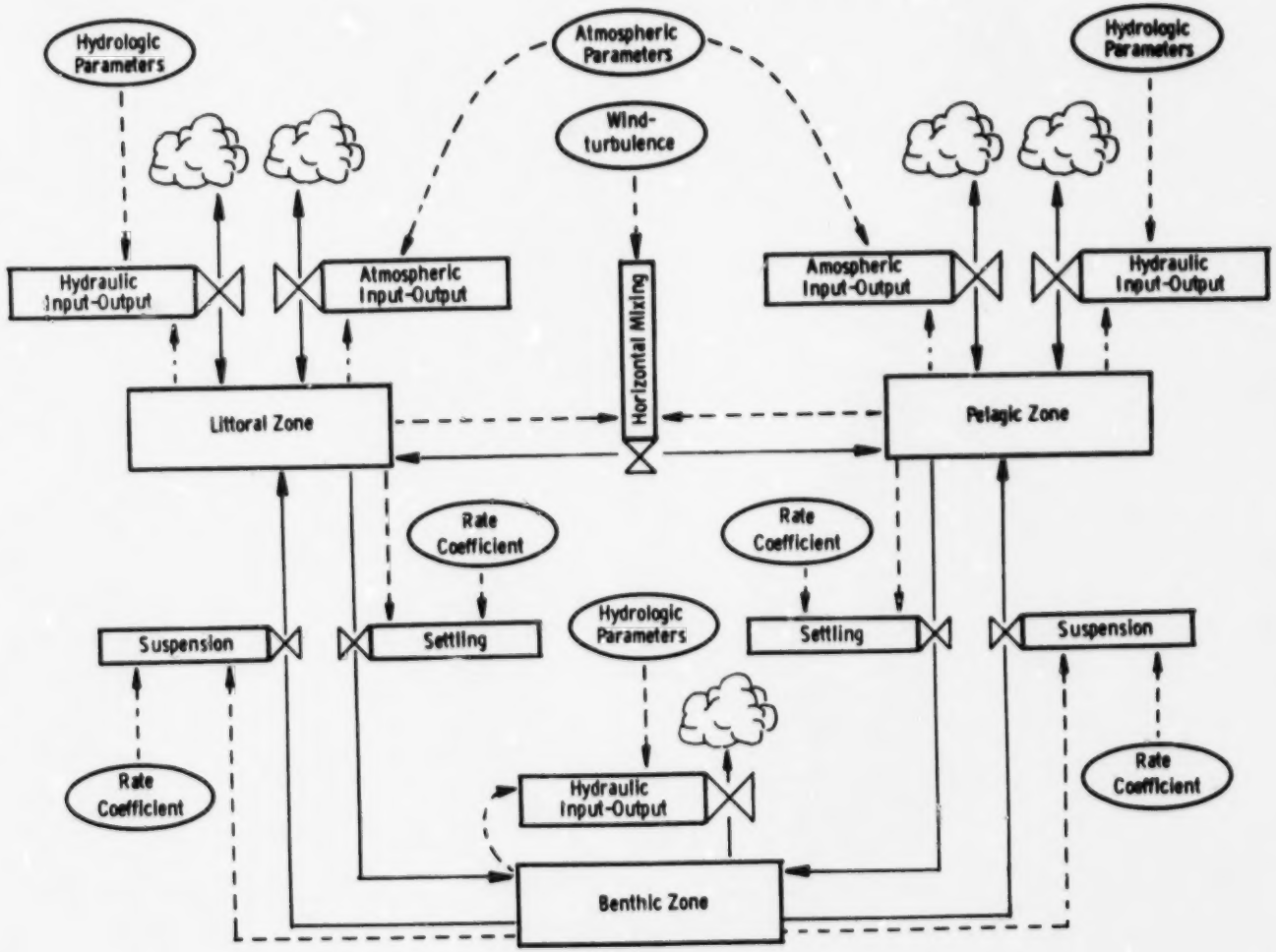


Figure 7: Horizontal Representation of a Lake.

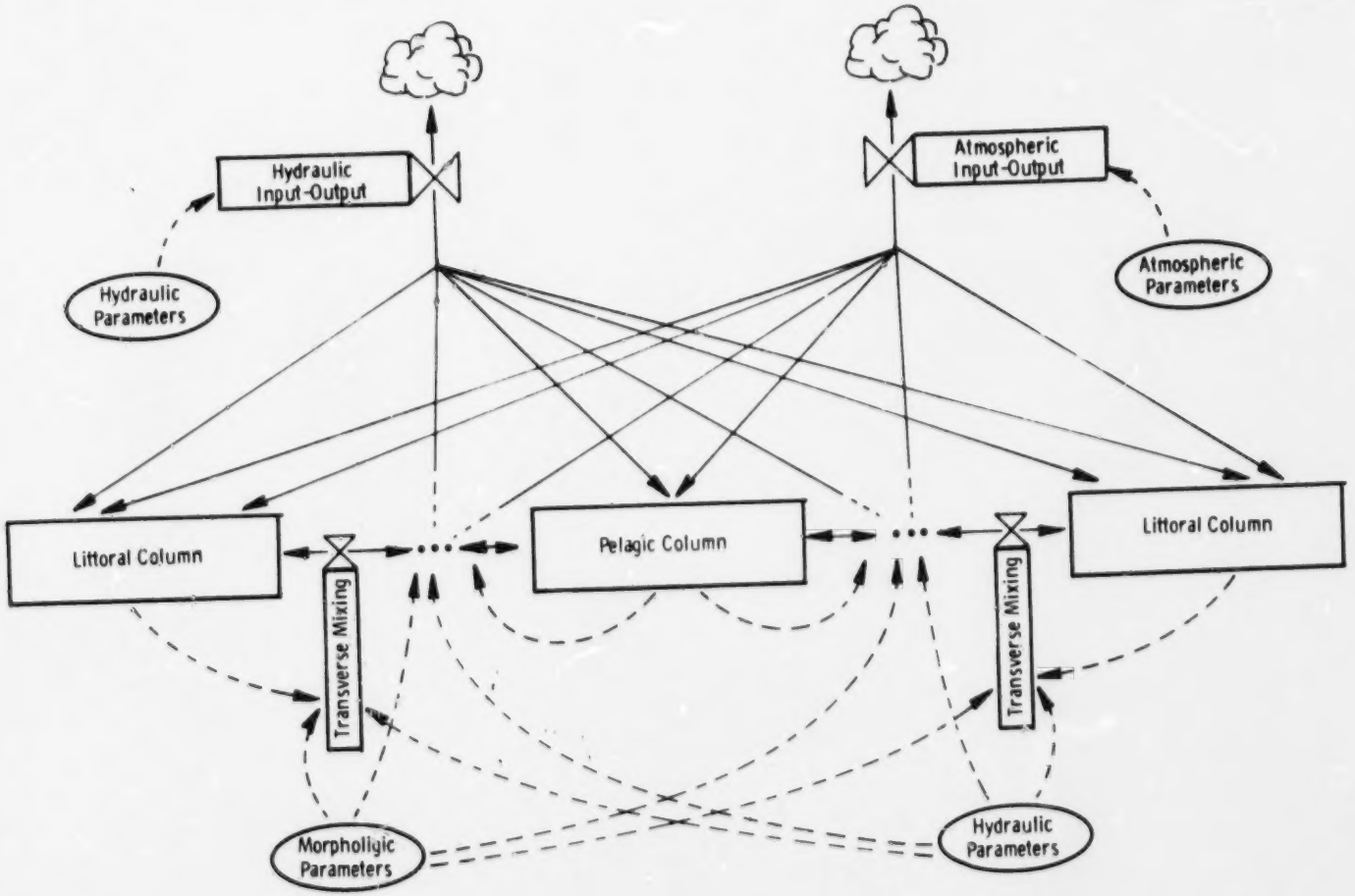


Figure 8: Horizontal Array of Vertical Columns for Representation of Lotic Systems.

In all of the preceding skeletal representations each storage component may be divided into discrete physical, chemical, and biological storage components with their associated transfers, rate coefficients, and coupled subsystems (e.g., food web biological uptake and storage with its associated growth, respiration, and trophic dynamics). A typical expansion of the surface layer storage component from the vertical representation of a lake in Figure 6 is shown in Figure 9.

Inputs and outputs may be expanded in a manner similar to the storage based upon their physical and chemical characteristics (dissolved, particulate, or absorbed). Expansion of the storage compartments may be necessitated by expansion of the hydraulic input-output to the epilimnion (Figure 10) into three separate inputs and outputs.

The storage labeled "Food Web" in Figure 9 is at the heart of most problems concerning pesticides in the environment (MOORE, 1967). A skeletal abstraction of a food web structure is shown in Figure 11 (compare to Figure 3). One method of allowing for the influence of food web dynamics upon the pesticide storages and fluxes in the model is to assume that the biomass levels in the aggregates representing the food web are at a steady state. Under this assumption the influence of the food web may be included in rate coefficients that affect the flux of pesticide between storage components representing pesticide concentration in the food web compartments. This is exemplified in the compartment diagram for the linear, donor-controlled model of DDT in the freshwater marsh of Figure 12.

Another method of allowing for the effects of the food web on pesticide behavior is to couple the explicit representation of the food web to the related pesticide storages. Thus, there will be two storage components coupled together in a manner similar to that of

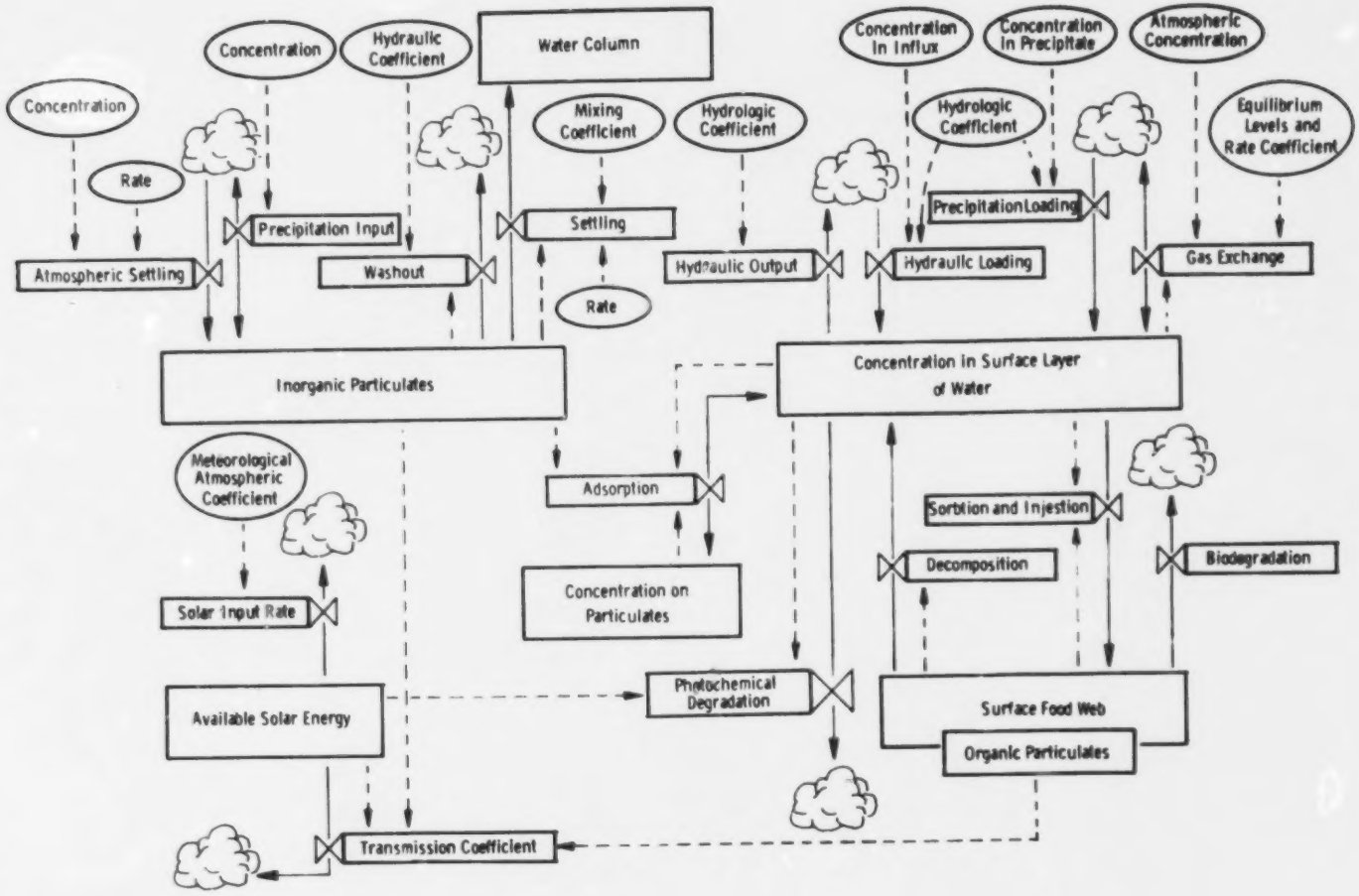


Figure 9: Some of the Storages, Processes, and Subsystems Associated with the Surface Layer Storage Compartment.

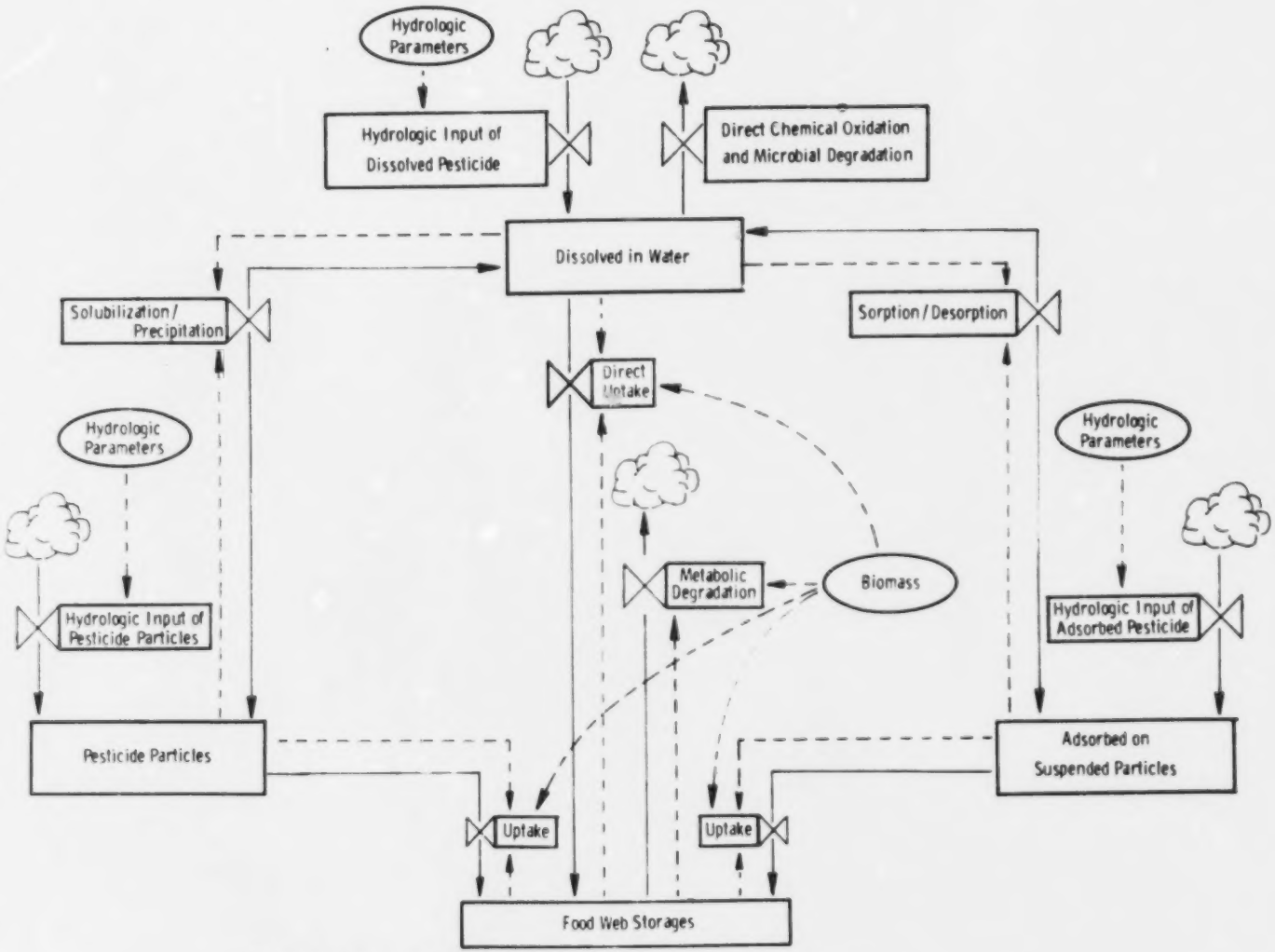


Figure 10: An Expansion of the Hydrologic Input.

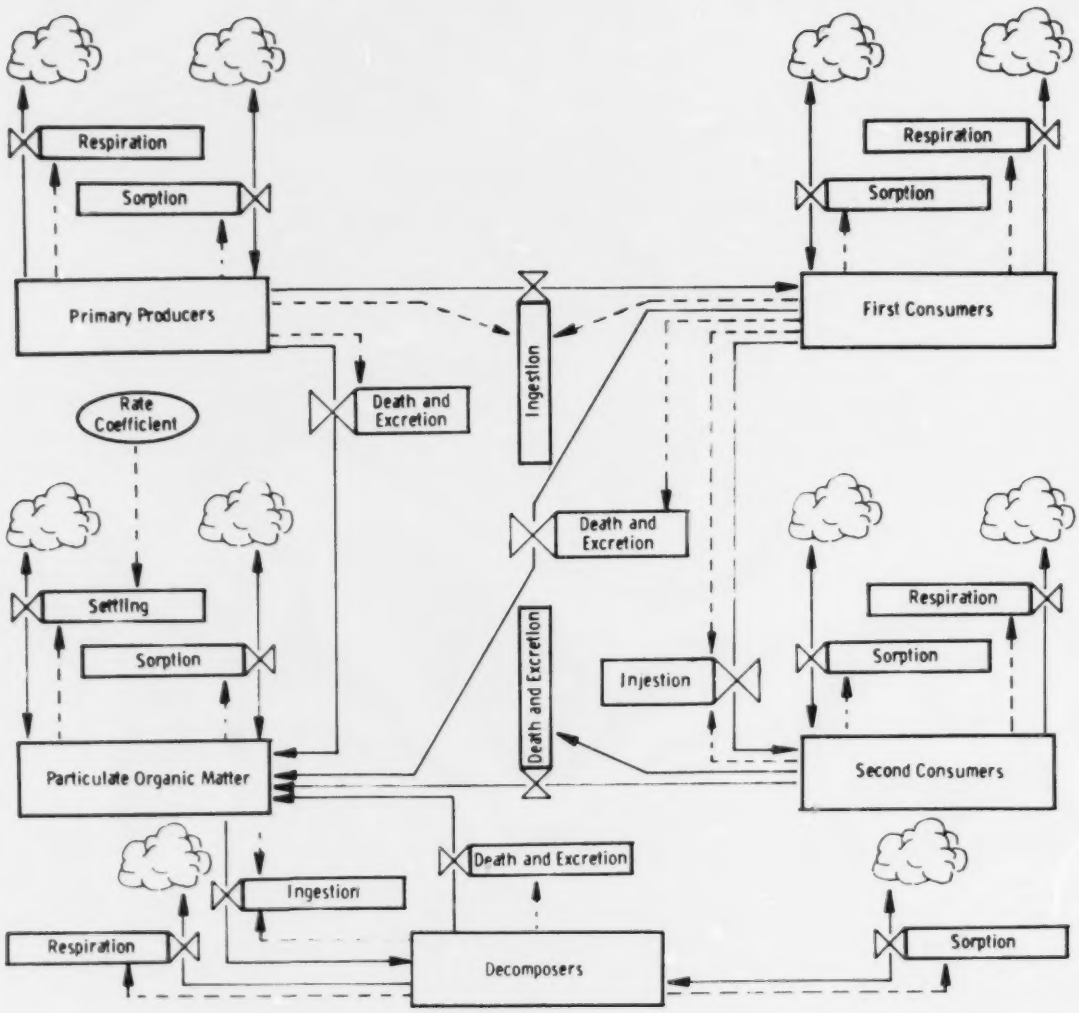


Figure 11: A Skeletal Abstraction of a Food Web.

Figure A-5 (see Appendix) for each storage of pesticide in a biotic component. The mathematical representation of this type of interaction is presented by HARRISON et al., (1971).

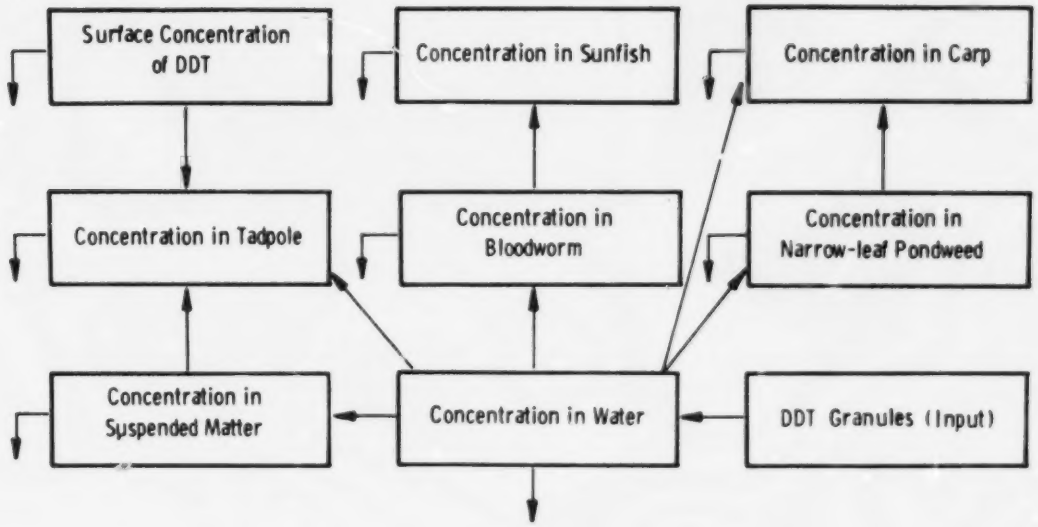


Figure 12: Food Chain Model of DDT in a Freshwater Marsh (from EBERHARDT et al., 1971).

Remembering that there is no best or correct representation, a plausible general model for a pesticide in the aquatic environment based upon the vertical skeletal structure is presented in Figure 13, an example of the result of the process of expanding the diagrams to include the system storages or processes that may be considered important. The system processes included in Figure 13 are intended to constitute a minimal set of parameters to be considered when investigating the movement and impact of a pesticide in the aquatic environment.

In a typical mathematical representation, which may be derived from the system diagram, each of the storage blocks accounts for one of a set of simultaneous differential equations. Also, each of the valve symbols accounts for a rate term in the set of equations. In addition, the coefficients or parameters in circles (many of which are omitted from Figure 13 for the sake of visual simplicity, e.g., pH, temperature, and Eh) appear as rate modifying coefficients in the equations. Each of these coefficients must be estimated from the literature or determined by a set of measurements on the system. Thus even the minimal set of variables of Figure 13 results in a complicated set of mathematical equations and requires a large data base for evaluation.

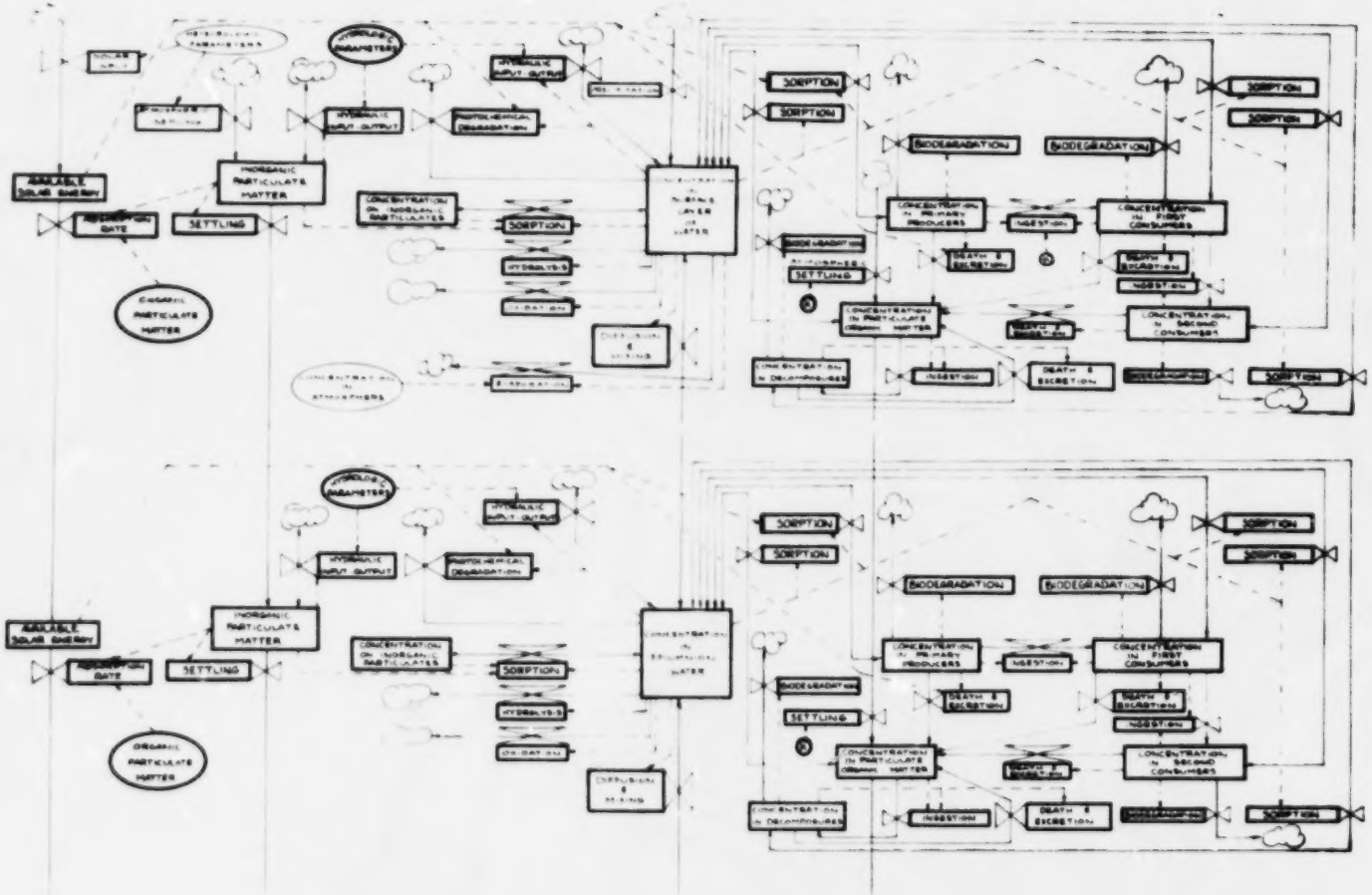
This complex representation can be reduced by aggregation of the least important variables for a particular pesticide and ecosystem. The inclination to eliminate the least important variables is usually intuitively focused either on very rapid processes, "which cannot be rate limiting," or conversely on very slow processes, "which cannot transport or transform much matter or energy," depending upon the investigator's objectives. The possible dangers in using these bases for eliminating variables lies in the synergistic behavior of causally closed environmental systems.*

The effect of an individual process on system behavior is dependent upon four levels of system interactions. These are

a. the rate coefficients and parameters for the process itself;
b. the hypothesized topology for the system interactions as presented in the system diagram;

---

*An ecosystem is a completely connected system (COMMONER, 1971) that is closed in the control sense (HUTCHISON, 1948; PATTEN, 1973). A closed control system or feedback system may exhibit "emergent properties" (CANNON, 1967) or "synergistic effects" (ODUM, 1971) that are dependent upon system structure or total system properties (BERTALANFFY, 1968). These properties can affect the influence of a specific process upon system behavior.


SORPTION
BIODEGRADATION
SETTLING
INGESTION
DEATH & EXCRETION

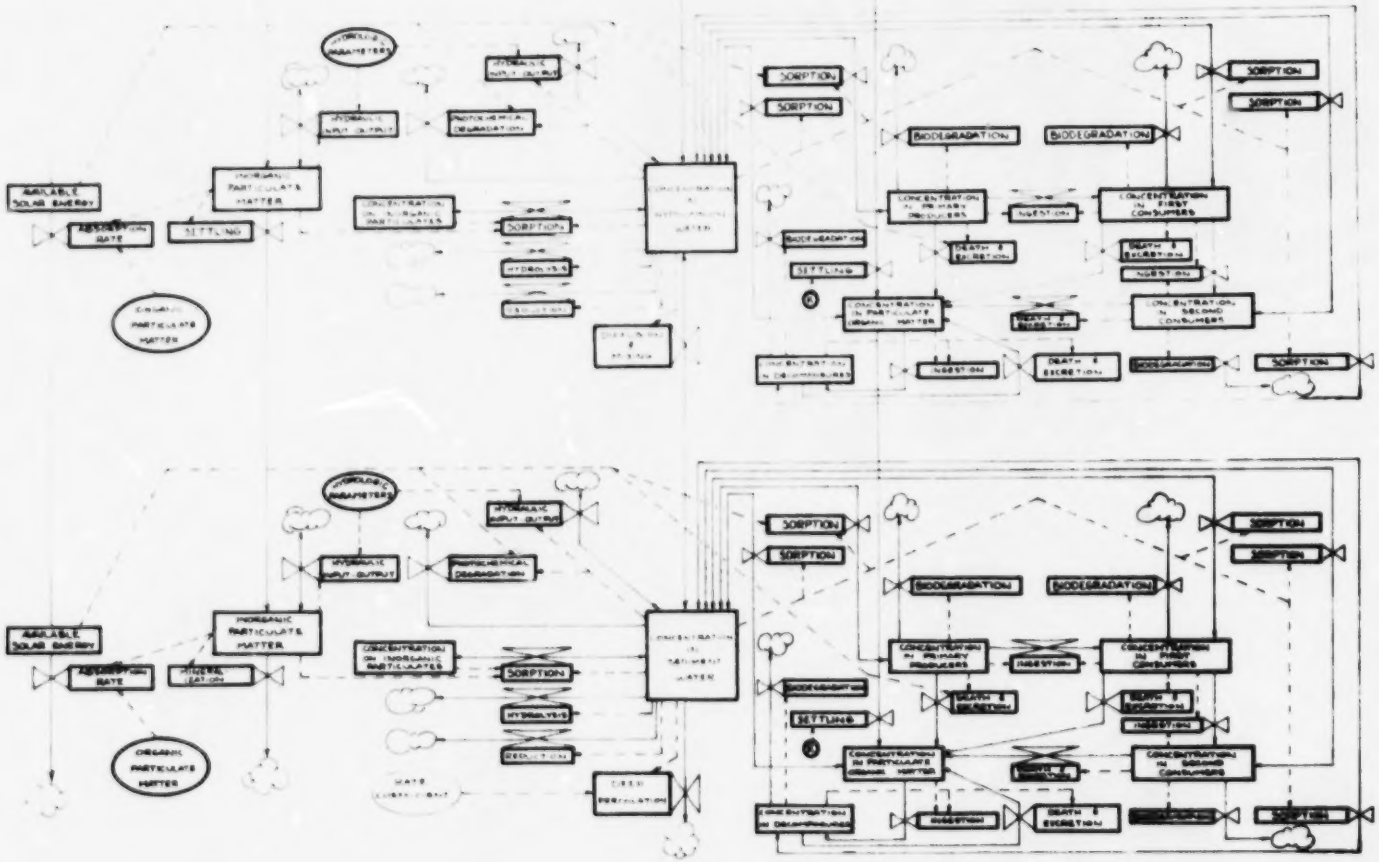


Figure 13: A Minimal Representation for a Pesticide in a Dimictic Lake.

c. the hypothesized system structure, which includes the influence of other process rates acting through the causal topology; and

d. the time series of inputs to the system.

Analytical techniques for estimating the effects of individual processes on the system behavior are summarized in Section I. The results provide an analytical basis for reduction of complex system diagrams.

SECTION VII
THE ESTUARINE/MARINE MODEL

The considerations incorporated in the freshwater aquatic model continue in relevance and validity into the estuarine/marine system, which can be viewed as specialized iterations of the general model (Figures 1 and 3). The relationship to the terrestrial and freshwater systems have been alluded to earlier (Figure 2). Thus, it is sufficient here to outline the significant differences and inter-relationships applicable to these regions of the environment.

The physical state of a compound in a system depends on its relation with the other components of the system, a behavior which can ideally be described by distribution constants when at equilibrium. For instance, the pharmaco-dynamic action of many drugs depends on their relative ability to bind to different sites. In such a fashion, the bloodstream may act as a reservoir permitting slow release of a drug to assure its long-term action. This ability to bind substances can occur anywhere. The toxicity of a pollutant must thus be evaluated in terms of the physical state(s) in which it shows toxicity and not merely by its observed concentration. With regard to availability to a carnivore, a pollutant adsorbed to detritus may be as unavailable as that adsorbed to a grain of sand.

Figure 14 is a schematic diagram of flow of a chemical through an estuary. It should be pointed out strongly that the estuarine system is exceedingly complex and any simulation will require time and caution.

Figure 15 is a representation of functional interactions at the interfaces between the estuary and other indicated ecosystems. The arrows indicate possible flux of chemicals without regard to form and origin. Interactions in the estuary are treated in a more precise conceptual fashion in Figure 14.

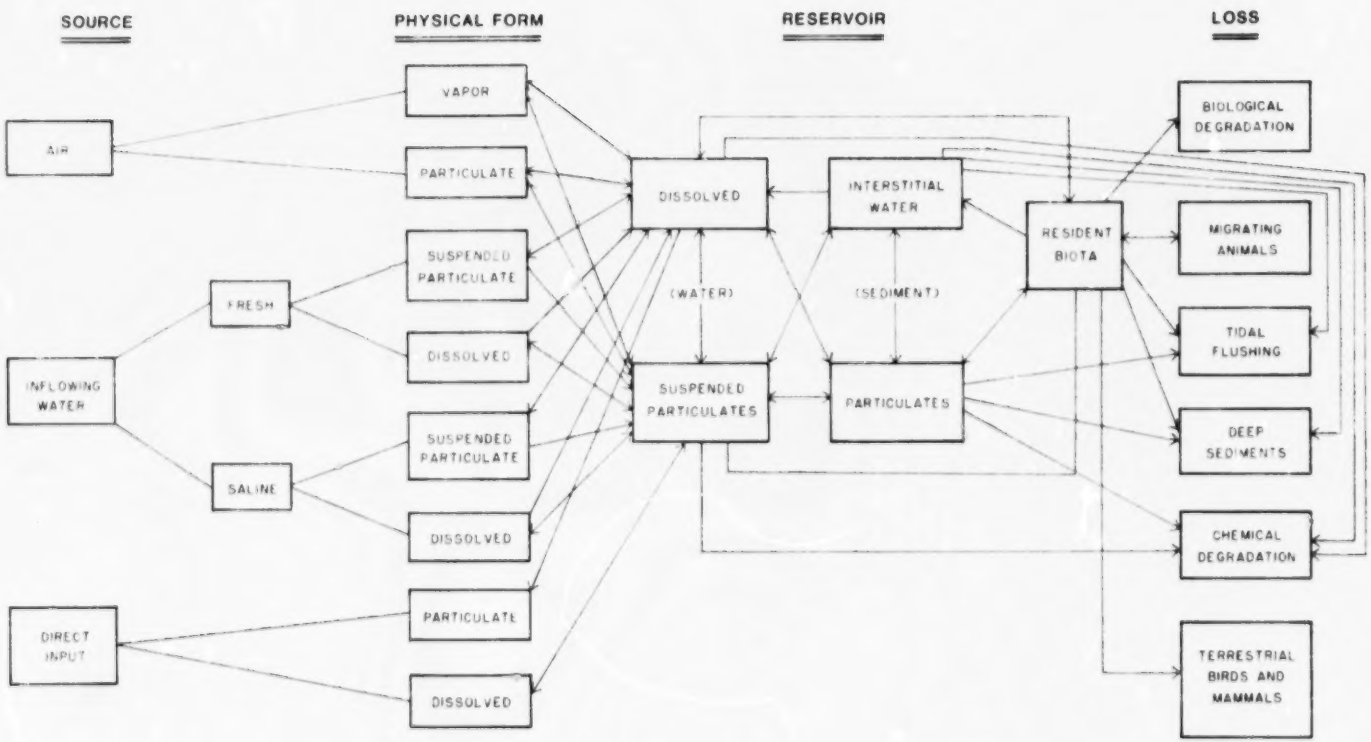


Figure 14: Simple Model of Transport in Estuaries.

The following definitions apply to Figure 15 only:

Run-off: Any transport from land adjacent to an estuary, including drainage not covered by river flow, such as non-specific drainage from swamps.

Tidal action: Any transport mediated by tidal flushing and tidal currents.

Biota-mediated flux: Any transport of organisms from one domain (sea coast, ocean, and fresh water) to another, such as in the case where a predator leaves its domain to feed in another domain, possibly itself becoming prey, or contamination through excretions (feces, urine, and regurgitated pellets). Emigration and immigration are also included.

River flow: Any transport mediated by a river or rivulet. This includes adsorbed as well as non-adsorbed materials.

Atmospheric disturbances: 1) Any transport caused by unusually high tides due to strong winds. 2) Any transport caused by agitation of the sediment or shore/bank by abnormally strong wave action or currents due to strong winds.

Turbulence: Any transport due to abnormal mixing caused by eddies (underwater storms).

Tides and Currents: Any transport due to normal tides and currents.

Fall-out: Any transport via the atmosphere.

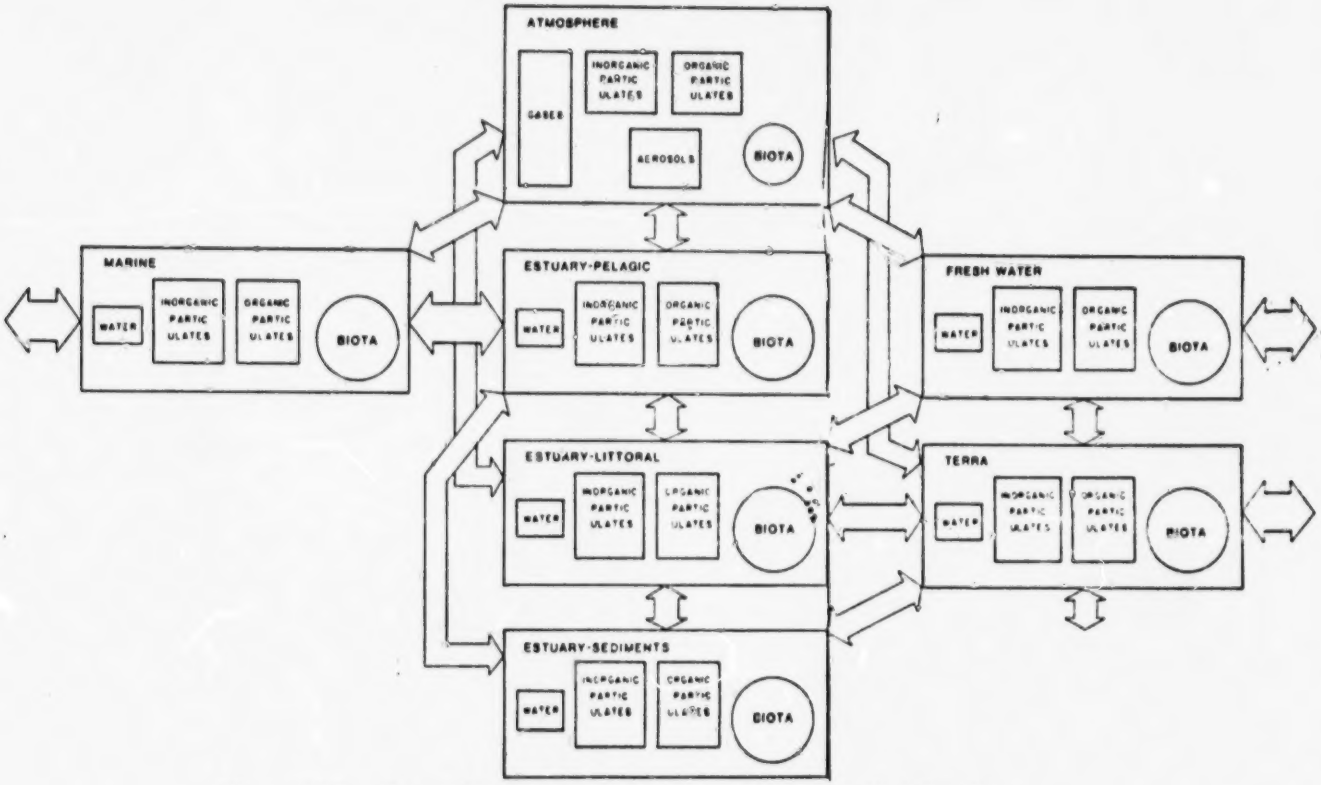
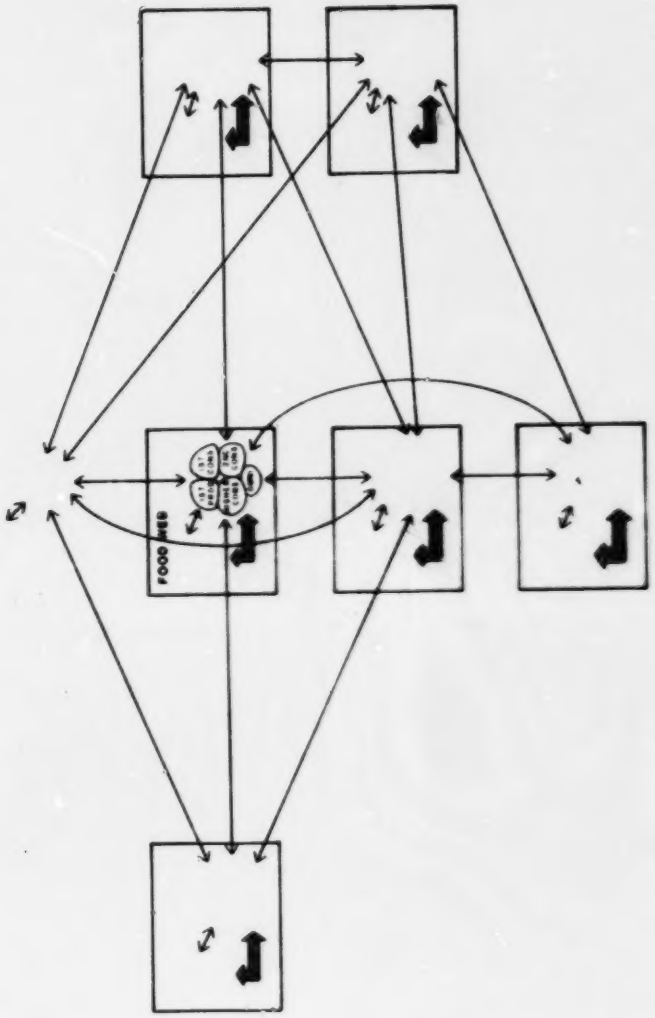


Figure 15: Expanded, Iterated Basic Chemical Module for Transport of Chemicals in Estuaries.

Open arrows indicate transport between modules via Run-off, River flow, Tidal actior, Turbulence, Fallout, and Atmospheric disturbances.

Biota-mediated Flux (overlay).
Solid arrows indicate unspecified migration, predation, life cycle-related changes, and transport-dependent movement between food webs associated with chemical modules representing environmental regions.



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Water Research (Monthly).

Weed Science. Amer. Weed Soc. (Bimonthly).

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Biological Abstracts (Semi-monthly).

Chemical Abstracts (Weekly).

Pesticide Abstracts (Monthly).

Sport Fishery Abstracts (Quarterly).

Water Pollution Abstracts (Monthly).

COMPUTER LITERATURE SEARCH DATA BASES

Medline (Biomedical) National Library of Medicine.

Toxline (Toxicology) National Library of Medicine.

WRSIC Water Resources Scientific Information Center

SIE Science Information Exchange. Smithsonian Institution, Washington, D.C.

NTI Search U.S. Department of Commerce.

ISI Institute for Scientific Information.

FEDERAL AND STATE RESEARCH LABORATORIES WHERE BOTH DATA AND INTERPRETATION OF DATA IS AVAILABLE

National Water Quality Laboratory. Pesticide Research Team. Mr. John G. Eaton, Coordinator. Duluth, Minnesota 55804.

Fish Control Laboratory, U.S. Bureau of Sport Fisheries and Wildlife, P.O. Box 862, LaCrosse, Wisconsin 54601.

Fish-Pesticide Research Laboratory, Bureau of Sport Fisheries and Wildlife, Route 1, Columbia, Missouri 65201.

Radiation and Metabolism Laboratory, U.S. Department of Agriculture, Fargo, North Dakota 58102.

Gulf Breeze Environmental Research Laboratory, Sabine Island, Gulf Breeze, Florida 32561.

Newtown Fish Toxicology Station, U.S. Environmental Protection Agency, 3411 Church Street, Cincinnati, Ohio 45244.

Southeast Environmental Research Laboratory, U.S. Environmental Protection Agency, College Station Road, Athens, Georgia 30601.

Perrine Primate Laboratory, Wenatchee Research Section, U.S. Environmental Protection Agency, P.O. Box 73, Wenatchee, Washington 98801.

U.S. Environmental Protection Agency Laboratory, Region 10, 15345 N.E. 36th Street, Redmond, Washington 98052.

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Gulf Coast Water Supply Laboratory, U.S. Environmental Protection Agency, P.O. Box 158, Dauphin Island, Alabama 36528.

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Fish Control Laboratory, U.S. Bureau of Sport Fisheries and Wildlife, Route 1, Box 9, Warm Springs, Georgia 31830.

Southeastern Fish Cultural Research Laboratory, U.S. Bureau of Sport Fisheries and Wildlife, Marion, Alabama 36756.

U.S. Environmental Protection Agency, Pesticide Monitoring Laboratory, Bay St. Louis, Mississippi 29520.

Great Lakes Fishery Laboratory, Bureau of Commercial Fisheries, Fish and Wildlife Service, U.S. Department of the Interior, Ann Arbor, Michigan 48107.

Wisconsin Department of Natural Resources, P.O. Box 450, Madison, Wisconsin 53701.

Agricultural Research Service Laboratories (U.S. Department of Agriculture) Regional.
(Studies on nuisance aquatic insecticides, herbicides, etc.)

Department of Defense, Naval Ship Research and Development, Center, Annapolis, Maryland 21402.
(Anti-Fouling Agents)

National Agricultural Library, U.S. Department of Agriculture, Beltsville, Maryland 20705.

Alaska Department of Environmental Conservation, Pouch O, Juneau, Alaska 99801.

Conservation Library Center, Denver Public Library, 1357 Broadway, Denver, Colorado 80283.

Division of Pesticide Community Studies, Office of Pesticide Programs, Environmental Protection Agency, 4770 Buford Highway, Chamblee, Georgia 30341.

Gulf South Research Institute, P.O. Box 1177, New Lberia, Louisiana 70560.

Fish Control Laboratory, U.S. Bureau of Sport Fisheries and Wildlife, Route 1, Box 9, Warm Springs, Georgia 31830.

Fish Farming Experimental Station, U.S. Bureau of Sport Fisheries and Wildlife, Box 860, Stuttgart, Arkansas 72160.

National Agricultural Chemicals Association, 1155 15th St. NW, Washington, D.C. 20005.

Division of Biology and Agriculture, National Research Council, 2101 Constitution Ave. NW, Washington, D.C. 20418.

New Hampshire Pesticides Control Board, State House Annex, Room 201, Concord, New Hampshire 03301.

New York State Department of Environmental Conservation, 50 Wolf Rd., Albany, New York 12201.

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Division of Wildlife Services. Bureau of Sport Fisheries and Wildlife. U.S. Department of the Interior, 1717 H Street NW, Washington, D.C. 20240.

Denver Wildlife Research Center. U.S. Bureau of Sport Fisheries and Wildlife, Building 16, Federal Center, Denver, Colorado 80225. from FLOR

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Department of Environmental Health, University of Cincinnati College of Medicine, Cincinnati, Ohio 45219.

Biological Sciences Library, University of New Hampshire, Kendall Hall, Durham, New Hampshire 03824.

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College of Forest Resources. University of Washington, Seattle, Washington 98105.

SOME PRIVATE CORPORATIONS HAVE PERFORMED
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Union Carbide Corporation, Tarrytown Technical Center, Tarrytown, New York 10591.

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Syracuse University Research Corporation, Merrill Lane, University Heights, Syracuse, New York 13210.

APPENDIX

GRAPHIC REPRESENTATION OF PESTICIDES IN AQUATIC SYSTEMS

In approaching any problem, an investigator must first form a mental image or conceptual model of the system. This conceptual model usually is not well defined and varies considerably from one investigator to another. With the complex problems associated with environmental systems, solving and/or communicating the conceptual model requires translation into the nonempirical language of mathematics or symbolic logic.

Since direct translation of the conceptual model into mathematical representation is awkward and difficult, the initial description is best formulated into a graphic symbolism. The nature of the graphic description is dependent upon the investigator's conceptualization of the processes, the degree of resolution required, and data that are available or that can be measured from experiments with the system. The graphical representation is the heart of systematic experimental design because the applicability of the ensuing analysis is limited by the ability of the investigator to represent his conceptual model of the system processes in graphic form. There is no best or correct graphical representation of a system. They differ only in the degree of realism and utility.

Graphical representations can be improved by iteration. After application of analytical techniques, any unusual or unexpected storage levels or flow rates may require modification of the components or connectivity of the original graphical representation. The nature of the iterative interactions among the graphical representation, the mathematical model, and data acquisition is presented in Figure A-1.

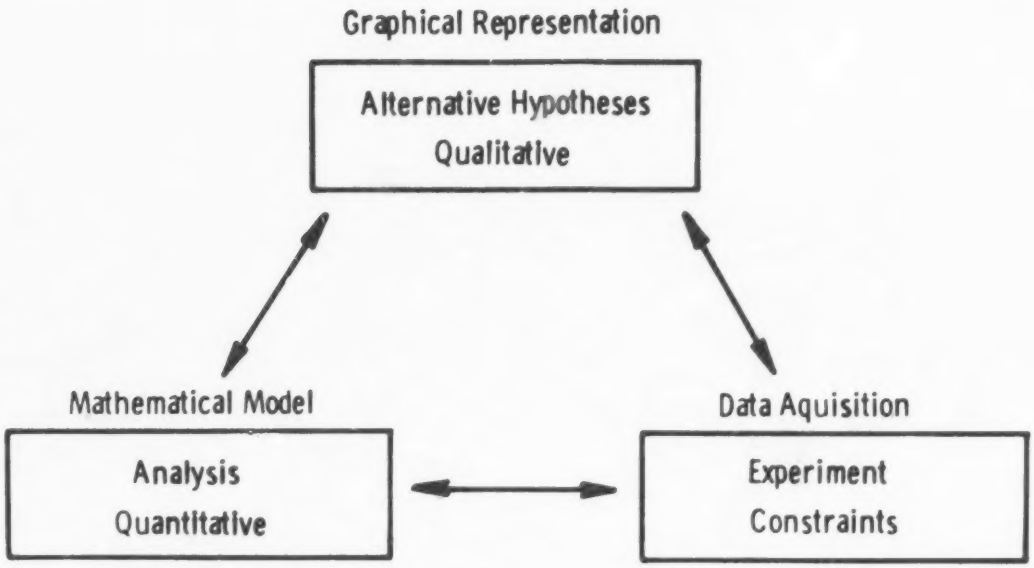


Figure A-1: Relationship Among Graphical Representations, The Mathematical Model and Data Acquisition (from QUINLAN, 1974).

Circuit diagrams (CLOSE, 1963) compartment diagrams (ODUM, 1971), block diagrams (KUO, 1962) signal flow graphs (KUO, 1962), bond graphs (KARNOPP and ROSENBERG, 1968), energy circuit language (ODUM, 1962), and Forrester diagrams (FORRESTER, 1971; MEADOWS et al., 1972) are all examples of graphical representations of systems. Each has advantages and disadvantages depending upon the nature of the system to be described.

Bond graphs are excellent symbolic representations for environmental systems in which energy flow is of primary concern and in which complementary variables (a potential and a related flux) may be defined. Compartment diagrams are useful representations of

environmental systems when mass or energy storage and their rates of exchange are of interest but complementary variables are not explicitly defined (ULANOWITZ, 1972). Signal flow graphs and associated control system analysis techniques are valuable when feedback control properties of the system are of primary concern. Forrester diagrams may be used in the general case to represent interactions, transformations, and transports of mass or energy without recourse to specific component equations or other constraints upon the system variables.

A Forrester diagram can be used to present a conceptual model of the transport and transformation of pesticides in the aquatic environment. From this presentation a reduced or working model in compartment form may be derived for a specific pesticide and specific ecosystem. The compartment diagram should include the mathematical form of the interactions and can provide a basis for preliminary system analysis as an aid to experimental design.

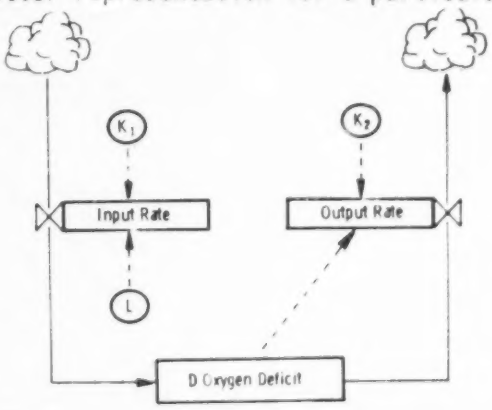
Forrester Diagrams

In Forrester diagrams of dynamic systems, six symbols are commonly used.

A solid line represents a directed pathway for transfer of matter or energy.
A dashed line represents a directed pathway for control or information transfer.
The cloud symbol represents a source or sink (input or output) outside the defined system boundaries.
A rectangle indicates storage of matter or energy.
The valve symbol indicates rates along the associated pathway.
Finally, the circle represents coefficients and parameters that affect flow rates.

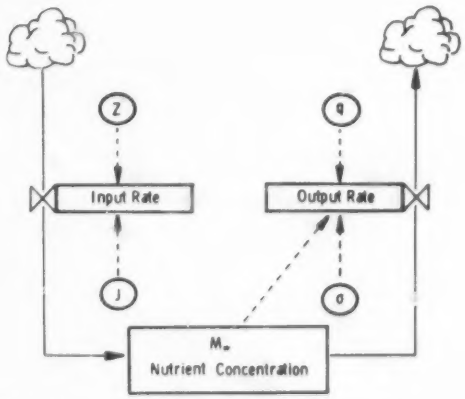
The degree of resolution or complexity of the Forrester diagram of a

system may vary considerably depending upon application and resources available for evaluating the hypothesis. While there appears to be no upper limit to the resolution of a model, the lower limit (a single storage component) is demonstrated for a stream and a lake in the following examples (Figures A-2 and A-3) from O'MELIA (1972). The low level of resolution in these examples does not necessarily imply that there is a better representation for a particular application.



$\frac{dD}{dt} = K_1L - K_2D$ where D = oxygen deficit, L = BOD remaining,
K_1 = deoxygenation coefficient, and
K_2 = reaeration coefficient.

Figure A-2: Streeter-Phelps Oxygen Deficit Model for a Stream.



$\frac{dM_w}{dt} = \frac{J}{Z} - (\sigma + q)M_w$ where M_w = concentration of nutrient,
J = flux of M to lake,
σ = sedimentation coefficient,
q = flow coefficient, and Z = mean lake depth.

Figure A-3: Vollenweider Lake Eutrophication Model.

One manner of increasing the resolution of a model is to divide a single storage component into sub-units, which may have differing rates of input or output for the stored variable. For example, the nutrient concentration in the lake (Mw) from Figure A-3 may be divided between abiotic storage (Ma) and biotic storage (Mb) with the result shown in Figure A-4. If the output rate (from sedimentation and flow) of the nutrient stored in the biotic component differs from that of the nutrient stored in the abiotic component, then the mean residence time is changed and the dynamic behavior of the nutrient output may be changed considerably from the single storage representation.

Another means of increasing the resolution of the representation is to include a time-varying parameter instead of the mean value of an exogenous variable that controls a rate of flow for an endogenous variable. Thus, instead of a mean lake depth (Z), a time varying lake depth [Z(t)] could be incorporated in the model.

Finally, the rate controlling flow and storage may be explicitly included in the representation and the two resulting subsystems can be realistically coupled (HARRISON et al., 1970). This is demonstrated in Figure A-5 for the biotic component of the lake model in Figure A-4. These expansions of the diagrams may continue until the point of diminishing returns is reached with respect to either application or resources.

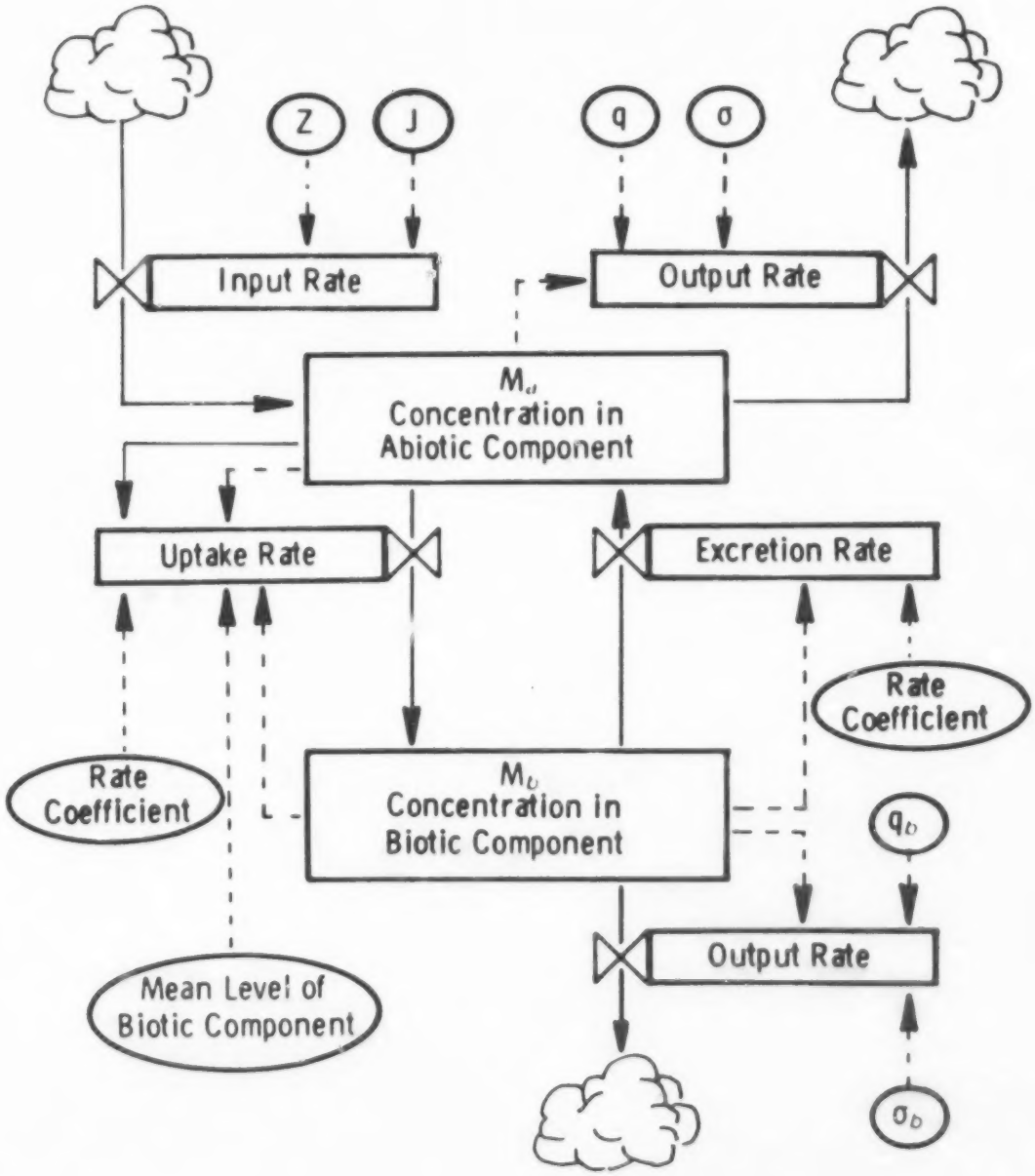


Figure A-4: Nutrient Model for Lake with Biotic and Abiotic Storage.

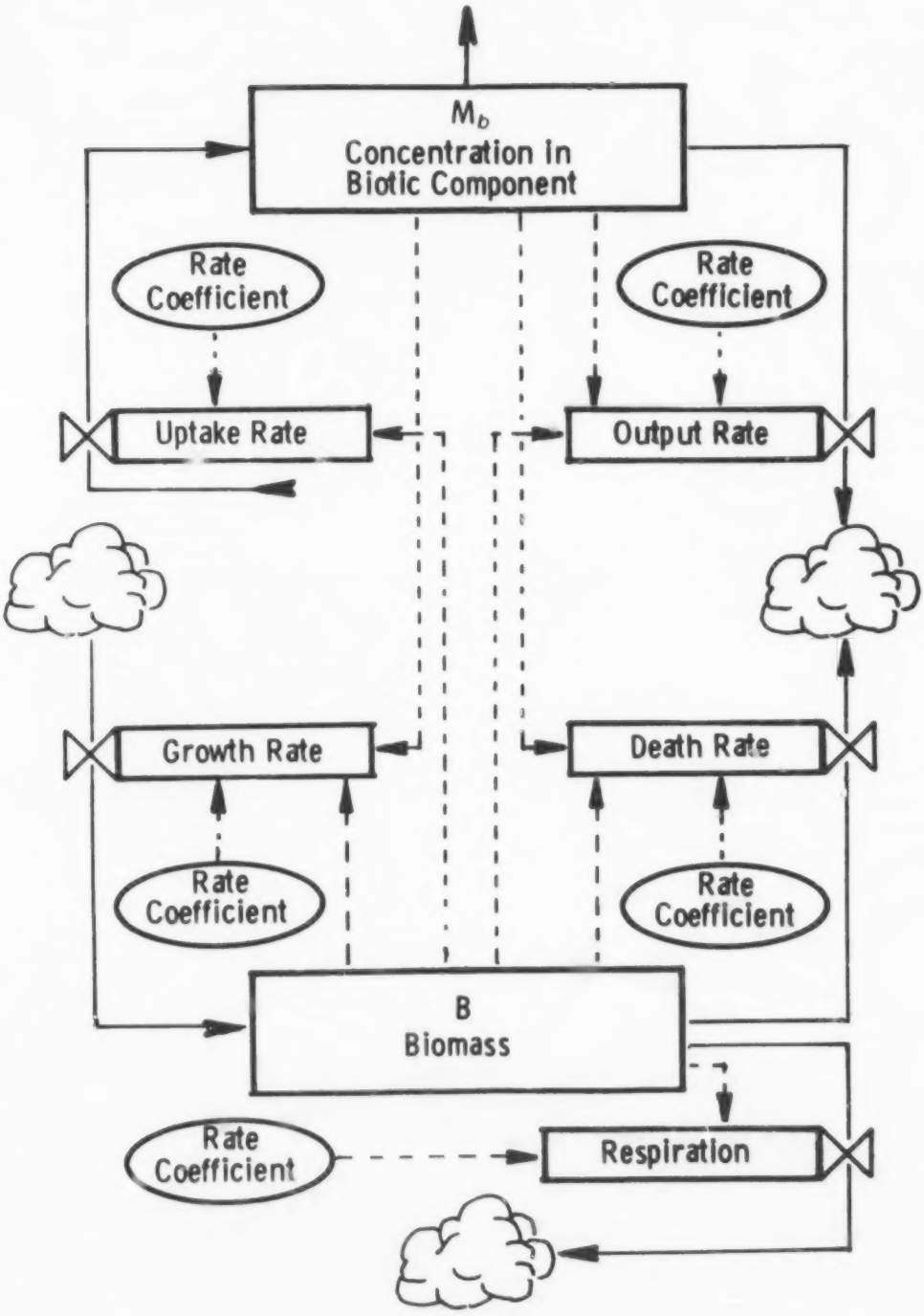


Figure A-5: Possible Coupling of Biomass (B) Subsystems with Nutrient Concentration (Mb) Subsystems.